

United States Air Force Research Laboratory



Lessons Learned Using Fractions To Assess Risk At Petroleum Release Sites

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//SIGNED//

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14. ABSTRACT Total petroleum hydrocarbon (TPH) fractional analysis and tiered risk assessments at petroleum release sites are replacing cleanup approaches based upon total TPH concentrations. Field demonstrations of the Total Petroleum Hydrocarbon Criteria Working Group (TPHSWG) approach for assessing human health risk at petroleum release sites were performed at eight Department of Defense installations. One site also provided an opportunity to demonstrate the Massachusetts Department of environmental Protection methodology and compare the approaches. Two lessons learned from the field demonstrations were: (1) TPH fractional analysis approaches provide a scientific bases for assessing risk and implementing appropriate criteria alone; and (2) the TPHCWG approach should not be used at relatively "fresh" petroleum product release sites because benzene, a know human carcinogen, is likely to be present at concentrations high enough to dominate cleanup decisions.						
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PREFACE

The field demonstrations for this project were performed by Operational Technologies Corporation (OpTech) under Contract Numbers F41624-94-D-9003/008, DAHA 90-06-D0014, DO TG01, F33601-01-F-9064 and F33601-02-F-A211. OpTech activities were conducted under the Project Management of Dr. Peter Lurker, 1370 North Fairfield Road, Suite A, Beavercreek, OH 45432. Dr. David Mattie of the Air Force Research Laboratory, Human Effectiveness Directorate (AFRL/HEPB) at Wright-Patterson AFB, OH, served as contract monitor. Teresa R. Sterner (OpTech) assisted in the preparation and editing of this report.

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The author also gratefully acknowledges the technical assistance and documentation that was provided by Dr. Martin Alexander, Department of Soil, Crop and Atmospheric Sciences, Cornell University, Ithaca, NY; Dr. Raymond C. Loehr, College of Engineering, The University of Texas at Austin; and Dr. David V. Nakles, Remediation Technologies, Inc. (RETEC), Monroeville, PA. Their continuing research into the fate of petroleum hydrocarbons in soil has greatly expanded both the depth and the breadth of understanding regarding bioavailability, sequestration, natural biodegradation processes and, ultimately, what concentrations of petroleum hydrocarbons in soil constitute an environmentally acceptable endpoint.

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LIST OF ABBREVIATIONS

AFB	Air Force Base
ASTM	American Society for Testing and Materials
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, xylenes
CCMS	Committee on Challenges to a Modern Society
CLARINET	Contaminated Land Rehabilitation Network for Environmental Technologies
DRO	diesel range organics
EC	equivalent carbon
EPA	Environmental Protection Agency
EPH	extractable petroleum hydrocarbons
FID	flame ionization detector
Ft	feet
GC	gas chromatograph
GC-MS	gas chromatograph-mass spectrophotometer
GRO	gasoline range organics
HBIL	health-based investigation level
IRP	Installation Restoration Program
JP	jet petroleum
kg	kilogram
K _{ow}	octanol-water partition coefficient
MADEP	Massachusetts Department of Environmental Protection
mg	milligram
mL	milliliter
NATO	North Atlantic Treaty Organization
NOAEL	no observable adverse effect level
OpTech	Operational Technologies Corporation
PAH	polycyclic aromatic hydrocarbon
PID	photoionization detector
POL	petroleum, oils and lubricants
PPRTV	Provisional Peer-Reviewed Toxicity Values
RBCA	Risk-Based Corrective Action
RBSL	risk-based screening level
RfC	reference concentration
RfD	reference dose
RISC	Risk-Integrated Software for Cleanups
SANGB	Springfield Air National Guard Base
TPH	total petroleum hydrocarbons
TPHCWG	Total Petroleum Hydrocarbon Criteria Working Group
UST	underground storage tank
VPH	volatile petroleum hydrocarbon

LESSONS LEARNED USING FRACTIONS TO ASSESS RISK AT PETROLEUM RELEASE SITES

EXECUTIVE SUMMARY

Petroleum release sites are problematic because petroleum mixtures are extremely complex. Manufactured petroleum products are composed of hundreds to thousands of aliphatic and aromatic compounds. Consequently, they are usually measured in environmental media as total petroleum hydrocarbons (TPH) using a variety of analytical techniques. Soil cleanup requirements based upon TPH concentrations have been established that range in value from a few mg of TPH per kg soil to tens of thousands of mg/kg. However, the TPH metric does not correlate to risk at petroleum release sites.

The Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) was convened in 1993 to "develop scientifically defensible information for establishing soil cleanup levels that are protective of human health at petroleum contaminated sites." This goal was established to address the large disparity among the states in soil cleanup requirements at sites that were contaminated with petroleum products such as gasoline, diesel fuel, jet fuel, heating oil, lubricants and used motor oils. The TPHCWG developed a methodology that defined TPH aliphatic and aromatic fractions within a tiered framework to assess the risk posed to human health at petroleum release sites. The TPHCWG used screening-level models and default inputs from the American Society for Testing and Materials (ASTM) *Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites* (RBCA) to illustrate calculation of risk-based screening levels (RBSLs) for applicable human health exposure scenarios.

This report summarizes the results of a series of field demonstrations that were performed at seven Department of Defense installations in the United States and one Air Force installation in Japan using the TPHCWG methodology. The field demonstrations were conducted at Misawa Air Base, Japan; El Toro Marine Air Station, CA; Tinker AFB, OK; Scott AFB, IL; Wright-Patterson AFB, OH; Elmendorf AFB, AK; Dobbins AFB, GA; and the Springfield Air National Guard Base (SANGB), OH. All eight field demonstrations were conducted between August 1998 and December 2002. Four of the demonstration sites were contaminated with jet fuel (i.e., JP-4, JP-5 or JP-8). The Misawa Air Base site was contaminated with a mixture of JP-4, JP-8, gasoline and diesel fuel. The Elmendorf AFB site was contaminated with diesel fuel, the El Toro site with both diesel fuel and heating oil, and the Tinker AFB site with JP-4 and diesel fuel. The last demonstration site (SANGB, Ohio), contaminated with JP-8, provided an opportunity to demonstrate both the TPHCWG approach and the Massachusetts Department of Environmental Protection (MADEP) methodology.

All field demonstrations included subsurface soil sampling. Soil sampling depths ranged from 1 to 101 feet below ground surface. Although the sites were markedly different in age, levels of TPH contamination, soil type, physical setting and history, they each provided a number of important lessons. Key lessons learned from these field demonstrations are as follows:

- TPH fractional analysis approaches, such as TPHCWG and MADEP, provide a scientific basis for assessing risk and implementing appropriate remedies at petroleum release sites, a process that cannot be achieved on the basis of TPH criteria alone.

- The TPHCWG methodology should not be used at petroleum release sites where relatively "fresh" products are involved because benzene, a known human carcinogen, is likely to be present at a concentration high enough to dominate cleanup decisions at such sites.
- TPH concentrations in site soils must be greater than 100 mg/kg, and preferably over 200 mg/kg, to effectively employ the TPHCWG approach at petroleum release sites.
- A soil volume of at least 125 mL is needed to support the fractional analysis of petroleum hydrocarbons in site soils using the TPHCWG methodology.
- Both the TPHCWG and MADEP approaches provide a TPH "fingerprint" that can be used to evaluate the consistency of TPH profiles across a petroleum release site. When the "fingerprint" is consistent across a site, less expensive conventional analyses (e.g., TPH-GRO (gasoline range organics) and TPH-DRO (diesel range organics)) can be used to fully characterize site contamination.
- The TPHCWG methodology is likely to underestimate total TPH concentrations at petroleum release sites when there are significant soil matrix effects (i.e., poor recovery of petroleum hydrocarbons from site soils).
- Unless the applicable guidance is strictly followed, the MADEP methodology is likely to overestimate total TPH concentrations at petroleum release sites, especially if the petroleum contaminant is jet fuel, because of the analytical overlap between the C₉ - C₁₂ volatile petroleum hydrocarbon aliphatic fraction and the C₉ - C₁₈ extractable petroleum hydrocarbon aliphatic fraction. This analytical overlap does not occur in the TPHCWG's Direct Method.
- The analysis of soil samples obtained from petroleum release sites for TPH by conventional methods and for petroleum hydrocarbon fractions by the TPHCWG's Direct Method or the MADEP method should be performed by the same analytical laboratory.
- Portable photoionization detector (PID) readings obtained from fresh soil core samples generally provide a reasonably good indication of the TPH concentration in site soils.
- Using one-half of the detection-limit for petroleum hydrocarbon fractions that are not detected by the analytical laboratory can significantly bias Tier 1 RBSL calculations.
- Continuous cores are very informational for the initial soil borings and lithologic descriptions. These continuous cores allow the geologist(s) to identify any potential zones of high or low permeability, which would transmit contaminants more or less rapidly than the surrounding lithologies. In addition, continuous core information provides the geologist with visual identification of changes in the contaminant staining in the soil. This information is especially important for sites contaminated with petroleum hydrocarbons.
- The RBSLs calculated using the ASTM RBCA process are conservative. At sites where this conservatism results in a questionable finding of significant risk to potential human receptors, a site-specific (i.e., Tier 2 and/or Tier 3) risk assessment is recommended.

The TPHCWG and MADEP methodologies provide similar results. Both approaches result in fractional analysis data that are likely to produce a similar TPH "fingerprint". Both also provide fractional results that can be used in a risk-based framework, such as ASTM RBCA, to assess the risk posed to potential human receptors by petroleum hydrocarbon contamination in site soils. However, the MADEP approach uses a reference concentration (RfC) for the lighter C₅ - C₈ aliphatic fraction that is nearly two orders of magnitude lower than the RfC used by the TPHCWG. Consequently, the MADEP methodology is likely to require more aggressive remedial measures at petroleum release sites, under some exposure scenarios, than those that would be indicated by the TPHCWG approach. Chronic toxicity studies of fraction-specific surrogate compounds or mixtures are needed to refine reference doses (RfDs) and RfCs for

aliphatic and aromatic hydrocarbon fractions and ensure consistency among the various fractional analysis methodologies already in use or under consideration.

Although the states of Louisiana, Oregon, Texas and Washington have formally adopted the TPHCWG methodology, at least seven other states are using a fractional analysis approach and a RBCA process to make cleanup decisions at petroleum release sites. International interest in the TPHCWG methodology and the RBCA process is also growing. Four provinces in Canada, the Commonwealth of Australia and the United Kingdom are using the TPHCWG methodology and the RBCA process to develop their own method for addressing risk and evaluating remedies at petroleum release sites within their borders. Keen interest in using fractional analysis of petroleum hydrocarbons and the RBCA process is also evident within the North Atlantic Treaty Organization Committee on Challenges to a Modern Society and the Contaminated Land Rehabilitation Network for Environmental Technologies (CLARINET) consortium in Europe.

Fractional analysis of TPH and the application of risk-based analyses at sites contaminated with petroleum hydrocarbons are becoming the preferred approach because the process leads to more scientifically-based cleanup levels and remedial action decisions. A growing number of states and nations are adopting this approach or are developing variations of the TPHCWG or MADEP methodologies. Today the concept of TPH fractional analysis and the subsequent application of tiered risk assessment at petroleum release sites are rapidly replacing the petroleum hydrocarbon cleanup approach that is based upon total TPH concentrations alone.

During the past ten years, considerable research has been conducted to develop an understanding of the natural biodegradation processes in soil and the associated bioavailability of petroleum hydrocarbons to microbial processes within the soil matrix. This research shows that petroleum components and many other organic chemicals present in soil become less available due to interactions between the chemical compounds and the soil. The reduction in availability lowers the risk these chemicals pose to human and ecological receptors. This research also shows that as petroleum hydrocarbons "age" in soil, they progressively become less and less available for biodegradation or bioremediation by microorganisms, for uptake by animals or plants, and for toxicity to any living organism. This process is called sequestration.

Although research has greatly increased the level of understanding of the bioavailability and sequestration of petroleum hydrocarbons in soils, there are a number of critical needs for risk-assessments at petroleum release sites that require further research. These critical needs include: (1) the identification of chemical and soil properties that govern the availability of petroleum hydrocarbons; (2) research into additional mechanisms that affect the availability of hydrocarbons in soil; (3) the development of rapid and cost-effective test methods to determine the available petroleum hydrocarbons in soil; (4) the rate of release of hydrocarbons from impacted soil to the environment; and (5) the development of widely accepted oral default values for bioavailability of petroleum hydrocarbons in site soils.

BACKGROUND

Winston Churchill, at a critical turning point in World War II, stated, "This is not the end. It is **not** even the beginning of the end. But it is, perhaps the end of the beginning." Unrecognized in **the** early 1990s, but obvious in hindsight, is the fact that the United States was at the "end of the beginning" of the period in which government laws and regulations were considered the best approach to environmental protection. The high cost and slow pace of environmental restoration efforts made it clear that the nation was drowning in a self-imposed regulatory quagmire. Since then, environmental protection efforts have increasingly focused on risk assessment, risk management and risk-based corrective action to address environmental contamination¹.

The management of petroleum hydrocarbon-impacted sites is a particularly pesky problem in the United States. The primary management goal is to obtain "closure" of the sites; that is, to achieve a set of conditions that is considered environmentally acceptable and which will ensure that no future management action will be required at the site. The debate associated with site closure that centers on the definition of "how clean is clean" goes on with no clear resolution in sight. This debate occurs at the national level under the U.S. Environmental Protection Agency (EPA) Superfund program and at state and local levels whenever the remediation of a site is examined. The key issue in this debate is determining the concentration of a given contaminant that is acceptable from a human health and environmental risk standpoint². That concentration may be the analytical detection limit, the background value at the site, some action level based upon a no observable effect, or some other level that may or may not have a scientific basis.

Petroleum (as crude oil) and petroleum products (e.g., gasoline, diesel fuel, heating oil) are **very** complex mixtures that contain primarily hydrocarbons (compounds containing molecules of carbon and hydrogen atoms) and some non-hydrocarbons. The complexity of petroleum and petroleum products increases with carbon number. The heavier the mixture, the larger the number of possible compounds becomes. For example, there are only 75 combinations for molecules containing 10 carbons, but there are 366,319 possible combinations for molecules containing 20 carbons. It is impossible to identify all components, so petroleum and petroleum products are characterized in terms of boiling point range and effective carbon number. Regardless of the complexity, hydrocarbons comprise the majority of the components in most petroleum products and are the compounds that are primarily (but not always) measured as total petroleum hydrocarbons³.

There are many analytical techniques available that measure total petroleum hydrocarbon (TPH) concentrations in environmental media. However, no single method measures the full range of petroleum-derived hydrocarbons. Consequently, any given sample analyzed by different TPH methods may result in various TPH values. Interpretation of the analytical result depends on an understanding of the capabilities and the limitations of the selected method(s) applied. Furthermore, cleanup levels that are based upon TPH concentrations implicitly assume that the TPH value is an accurate measure of the petroleum-derived hydrocarbon concentration in the environmental media of concern, and that the TPH value clearly indicates the degree of risk associated with the level of contamination. These assumptions are not valid because of the variability in analytical techniques, the complex nature of petroleum-derived hydrocarbon products, and the changes in composition that occur over time due to weathering³.

The Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) was convened in 1993 to "develop scientifically defensible information for establishing soil cleanup levels that are protective of human health at petroleum contaminated sites". This goal was established to

address the large disparity among the states in soil cleanup requirements at sites that were contaminated with petroleum products such as gasoline, diesel fuel, jet fuel, heating oil, lubricants and used motor oils. At that time, most soil cleanup requirements were based upon TPH concentrations that ranged from a few mg/kg to tens of thousands of mg/kg TPH. The TPHCWG approach can be used within a tiered framework to estimate human health risk and to calculate risk-based screening levels (RBSLs)³. The TPHCWG approach is consistent with the U.S. EPA 1989 *Risk Assessment Guidance for Superfund*⁴ and the American Society for Testing and Materials (ASTM) E 1739 – 95, *Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites*⁵.

During the past decade the Gas Research Institute (GRI), the Petroleum Environmental Research Forum (PERF) and a number of soil scientists including Dr. Martin Alexander, Department of Soil, Crop and Atmospheric Sciences, Cornell University; Dr. Raymond C. Loehr, Hussein M. Alharthy Centennial Chair Emeritus, College of Engineering, The University of Texas at Austin; and Dr. David V. Nakles, Remediation Technologies, Inc. (RETEC), Monroeville, PA, have conducted extensive research into the fate of petroleum hydrocarbons in soil. Some of what these organizations and soil scientists have learned about the bioavailability, biodegradation and sequestration of petroleum hydrocarbons in soil is also included herein.

INTRODUCTION

This report summarizes the results of a series of field demonstrations that were performed at seven Department of Defense installations in the United States and one Air Force installation in Japan using the TPHCWG methodology. This report also describes the Massachusetts Department of Environmental Protection (MADEP) methodology, another petroleum hydrocarbon fractionation method, and discusses the many lessons learned from applying these fractional analysis approaches at petroleum release sites. This report also looks at the risk to human health and the environment posed by petroleum hydrocarbons in soils from the perspective of bioavailability, sequestration and aging effects.

The field demonstrations were conducted at Misawa Air Base, Japan; El Toro Marine Air Station, California; Tinker AFB, Oklahoma; Scott AFB, Illinois; Wright-Patterson AFB, Ohio; Elmendorf AFB, Alaska; Dobbins AFB, Georgia; and the Springfield Air National Guard Base (SANGB), Ohio. All eight field demonstrations were conducted between August 1998 and December 2002. Four of the demonstration sites were contaminated with jet fuel (i.e., JP-4, JP-5 or JP-8). The Misawa Air Base site was polluted with a mixture of JP-4, JP-8, gasoline and diesel fuel. The Elmendorf AFB site was contaminated with diesel fuel, the El Toro site with both diesel fuel and heating oil, and the Tinker AFB site with JP-4 and diesel fuel. The last demonstration site, SANGB in Ohio, provided an opportunity to demonstrate both the TPHCWG approach and the MADEP methodology. A summary of the field demonstration data is shown in Table 1 below. A site by site summary of the field demonstrations and their respective results can be found in Appendix A. A comparison of the TPHCWG and MADEP approaches is included in Appendix B and key terms are defined in the glossary, Appendix C.

Table 1: Summary of TPHCWG Field Demonstration Site Data⁶⁻¹³

Demonstration Site	Petroleum Contamination	Soil Type	Sampling Depth (ft bgs)	Number of Samples	TPH _f Concentration Range (mg/kg)
Misawa AB, Japan	JP-4, JP-8, gasoline & diesel	sand, silt & clay	20 - 33	9	700 - 12,000
El Toro Marine Air Station	diesel fuel & heating oil	sand & silt	5 - 101	15	<1 - 28,000
Tinker AFB, OK	JP-4 & diesel fuel	silt, loam & clay	1 - 11	7	41 - 10,700
Scott AFB, IL	JP-8	sand, silt & clay	8 - 9	5	<1 - 598
Wright-Patterson AFB	JP-8	silty loam	0.5 - 1	6	389 - 11,657
Elmendorf AFB, AK	diesel fuel	sand, gravel & silt	<2 - 12	10	111 - 1,682
Dobbins AFB, GA	JP-4, JP-5 & JP-8	sand & silty clay	1 - 8.5	15	12 - 9,339
SANGB, OH	JP-8	silty clay	4.5 - 5.5	10	<22 - 560

Note: bgs - below ground surface, TPH_f - total petroleum hydrocarbon fractions

The main objectives for each of the field demonstrations were as follows:

- 1 To effectively demonstrate the utility of the TPHCWG fractional analysis approach in TPH contaminated soil, regardless of fuel type, soil type, environmental setting or contaminant history.
- 2 To provide additional data on the characteristics of petroleum products in soil to support the development of a cost-effective site assessment program using the risk-based corrective action (RBCA) decision making process.
- 3 To enhance regulatory agency acceptance of risk-based approaches for assessing human health risks at petroleum contaminated sites in the United States using TPH fractional analysis methodologies.

SUMMARY OF TPHCWG FIELD DEMONSTRATION RESULTS

The TPHCWG field demonstration sites included three fuel storage areas (tank farms), six underground storage tanks (USTs) and one aircraft impact area. All field demonstrations included limited subsurface soil sampling, ranging in depths from 1 to 101 feet bgs. Although the sites were markedly different in age, levels of TPH contamination, soil type, physical setting and history, they each provided a number of important lessons that were learned from the demonstration. The key lessons that were learned from these field demonstrations are listed below.

- TPH fractional analysis approaches, such as TPHCWG and MADEP, provide a more scientific basis for implementing remedies at petroleum release sites than cleanup standards based upon TPH alone.
- The TPHCWG methodology should not be used at petroleum release sites where relatively "fresh" products are involved because benzene, a known human carcinogen, is likely to be present at a concentration high enough to dominate cleanup decisions at such sites.
- TPH concentrations in site soils must be greater than 100 mg/kg (and preferably over 200 mg/kg) to effectively employ the TPHCWG approach at petroleum release sites.
- A soil volume of at least 125 mL is needed to support the fractional analysis of petroleum hydrocarbons in site soils using the TPHCWG methodology.
- Both the TPHCWG and MADEP approaches provide a TPH "fingerprint" that can be used to evaluate the consistency of TPH profiles across a petroleum release site. When the "fingerprint" is consistent across a site, less expensive conventional analyses (e.g., TPH-DRO (diesel range organics) and TPH-GRO) can be used to fully characterize site contamination.
- The TPHCWG methodology is likely to underestimate total TPH concentrations at petroleum release sites when there are significant soil matrix effects (i.e., poor recoveries of petroleum hydrocarbons from site soils).
- Unless the applicable guidance is strictly followed (WSC-02-411)¹⁴, the MADEP methodology is likely to overestimate total TPH concentrations at petroleum release sites, especially if the petroleum contaminant is jet fuel, because of the analytical overlap between the C₉ - C₁₂ volatile petroleum hydrocarbon (VPH) aliphatic fraction and the C₉ - C₁₈ extractable petroleum hydrocarbon (EPH) aliphatic fraction. This analytical overlap does not occur in the TPHCWG's Direct Method.
- The same analytical laboratory should perform all analyses of soil samples, including TPH analyses by conventional methods and fractionation analyses by the Direct or the MADEP method.
- Portable photoionization detector (PID) readings of soil core samples taken immediately after collection generally provide a reasonably good indication of the TPH concentration in site soils.
- Using one-half of the detection-limit for petroleum hydrocarbon fractions that are not detected by the analytical laboratory can significantly bias Tier 1 RBSL calculations.
- Continuous cores are very informational for the initial soil borings and lithologic descriptions. These continuous cores allow the geologist to identify any potential zones of high or low permeability, which would transmit contaminants more or less rapidly than the surrounding lithologies. In addition, continuous core information provides the geologist with visual identification of changes in the contaminant staining in the soil. This information is especially important for sites contaminated with petroleum hydrocarbons.
- The RBSLs calculated using the ASTM RBCA process are conservative. At sites where this conservatism results in a questionable finding of significant risk to potential human receptors, a site-specific (i.e., Tier 2 and/or Tier 3) risk assessment is recommended.

These key lessons, and others that were learned from the TPHCWG field demonstrations, indicate that decision makers are likely to impose more appropriate cleanup measures at petroleum release sites when such sites are evaluated under a RBCA process using TPH fractional analysis approaches. For example, the TPH concentrations at the Elmendorf AFB site were clearly above the Alaska Department of Environmental Conservation's Method Two cleanup level of 250 mg/kg for migration to groundwater. However, TPH concentrations in site soils were typically below RBSLs for applicable exposure pathways at this site¹¹. At the Harrier

jet crash demonstration site near Wright-Patterson Air Force Base, TPH RBSLs were approximately four to seven times higher than Ohio action levels for residential land use¹⁰. This finding was fairly typical of the findings at other demonstration sites where RBSLs were generally above state cleanup criteria based upon TPH levels alone.

The lessons learned from the TPHCWG field demonstrations also confirmed the need for good site characterization data (i.e., the nature and extent of petroleum hydrocarbon contamination in site soils must be known/documented) and appropriate pre-planning prior to field sampling activities. Careful pre-planning, including the preparation of a site-specific work plan, helped ensure that sample collection activities provided an adequate number of samples with sufficient volume and TPH concentrations to enable the analytical laboratory to obtain the necessary TPH fractional analysis data.

The TPHCWG field demonstrations also made it clear that the Working Group approach, or any other TPH fractional analysis methodology, should not be applied at petroleum release sites where fresh or relatively fresh product is present. At such sites, the relatively high concentrations of benzene that are likely to be present will overshadow any risk that may be posed by the non-carcinogenic components of the petroleum product.

VPH/EPH OVERLAP IN THE C₉ – C₁₂ ALIPHATIC FRACTION

The tendency for the MADEP approach to overestimate TPH concentrations in the C₉ – C₁₂ aliphatic fraction was clearly evident at the SANGB demonstration site¹³. When the MADEP methodology is applied at sites contaminated with jet fuels, such as the JP-8 contamination that was present at this site, significant overlap in the concentrations detected in the C₉ – C₁₂ aliphatic fraction occurs between the VPH and EPH protocols. The MADEP designed the VPH and EPH protocols to focus on gasoline (VPH) and diesel fuel (EPH) spills, respectively. Consequently, for jet fuel mixtures such as JP-8, which is largely composed of C₉ through C₁₈ aliphatic hydrocarbons, the C₉ to C₁₂ VPH range will overlap with the aliphatic hydrocarbons in the C₉ to C₁₈ EPH range. When the petroleum hydrocarbon mixture has relatively high concentrations of C₉ through C₁₂ aliphatics (as in JP-8), the overlap can be significant, depending on the amount of weathering that has occurred within the soil matrix. When both the VPH and EPH analytical protocols are used to analyze a petroleum hydrocarbon mixture, MADEP guidance (policy number WSC-02-411) directs that the C₉ - C₁₂ aliphatic fraction concentration determined by the VPH method be ignored¹⁴. Thus, the actual C₉ - C₁₂ concentration is contained within the C₉ - C₁₈ range determined by the EPH method.

To evaluate the significance of the overlap in the C₉ - C₁₂ aliphatic fraction, the analytical data obtained from the field demonstration conducted at the SANGB site were subjected to a simple mathematical analysis as shown in Table 2 below. The average reduction in aliphatic hydrocarbon concentrations in the C₉ - C₁₈ range is about 70 percent across the 10 samples obtained from the JP-8 contaminated soils at the SANGB site, when the C₉ - C₁₂ VPH values are excluded. Consequently, the overlap in the C₉ - C₁₂ aliphatic hydrocarbon fraction is very significant. If the actual concentrations detected in the C₉ - C₁₈ fraction are those detected by the EPH method, adding the concentrations detected in the C₉ - C₁₂ fraction by the VPH method inflates the total concentration by a large margin (nearly a factor of two).

Table 2: VPH vs. EPH – Springfield Air National Guard Base

Soil Boring Number	B01	B02	B03	B04	B08	B09	B10	B12	B14	B15
C ₉ – C ₁₂ (VPH)	25.9	88.8	209	31.3	330	166	380	282	101	89
C ₉ – C ₁₈ (EPH)	6.4	16	93	19	100	210	140	70	46	59
Total	32.3	104.8	302	503	430	376	520	352	147	148
Actual ^a	6.4	16	93	19	100	210	140	70	46	59
% Reduction ^b	80	84.7	69.2	62.2	76.7	44.1	73.1	80.1	68.7	60.1

Note: ^aactual concentration = C₉ – C₁₈ (EPH) value; ^baverage % reduction = 69.9%

ENVIRONMENTALLY ACCEPTABLE ENDPOINTS IN SOILS

Another key lesson learned from the field demonstrations is that petroleum hydrocarbons can be present in soil at concentrations above established cleanup levels, yet pose no significant risk to human health or the environment. The GRI, as well as a number of other organizations and individuals, have been conducting research on the bioremediation of petroleum hydrocarbons in soil for more than a decade. To date the results of this extensive effort have shown that: (1) petroleum hydrocarbons are biodegraded by indigenous soil microorganisms to a concentration that decreases very slowly with time and/or continued treatment, (2) reductions below this concentration are limited by the availability of the petroleum hydrocarbons to the microorganisms, and (3) the residual petroleum hydrocarbons that remain after biological treatment, regardless of the extent of treatment, are significantly less leachable (in water) and significantly less available to other organisms as measured by simple indicator toxicity tests (e.g., earthworm mortality and Microtox™). In summary, the aged petroleum hydrocarbons in soil are less available to many organisms, resulting in less exposure and reduced toxicological effects, and are less prone to leaching compared to petroleum hydrocarbons that are freshly added to soils².

On the basis of these findings, the treatment of petroleum hydrocarbons in soils by bioremediation and/or natural degradation in the environment can reduce their concentrations to levels where they no longer pose an unacceptable risk to human or ecological receptors. It is now believed that the petroleum hydrocarbons that remain in treated soil are no longer available to microorganisms, other ecological receptors, or to humans, following bioremediation and/or natural biodegradation, and thus represent an environmentally acceptable endpoint in soils².

The research shows that petroleum hydrocarbons and many other organic chemicals present in soil become less available due to interactions between the chemical compounds and the soil and that the reduction in availability lowers the risk these chemicals pose to human and ecological receptors. Furthermore, availability of an organic chemical in soil is not a function of its measured concentration; rather, it depends upon the soil (e.g., sand versus clay; low versus high total organic carbon), chemical properties, and the time of contact between the chemical and the soil (i.e., aging), as well as the type and extent of treatment to which it has been subjected. The longer many organic chemicals are in contact with soil, the less amenable they become to extraction by solvents².

Biodegradation is the oxidation of hydrocarbons by microbial processes. The classification used to identify the extent of prior biodegradation in these soils was adopted from Moldowan *et al.*

(1992, as cited in Loehr *et al.* (2001)¹⁵), as shown in Figure 1 below. For this evaluation, soils were classified as the following in terms of the amount of biodegradation that had occurred: (1) slight = loss of n-alkanes; (2) moderate = loss of n-alkanes and some loss of isoprenoids and parent three-ring polycyclic aromatic hydrocarbons (PAHs); (3) severe = no n-alkanes and loss of isoprenoids and three-ring alkylated PAHs; and (4) very severe = loss of four-ring PAHs and prominent biomarker peaks in the gas chromatograph (GC) chromatogram¹⁵.

Exhaustive extraction frequently gives values for the concentrations of organic compounds that are somewhat or greatly different from the levels that are bioavailable or toxic. It is also likely that the extent of changes in bioavailability and toxicity associated with aging are often not directly parallel to the changes reflected by exhaustive extraction techniques prior to chemical analysis².

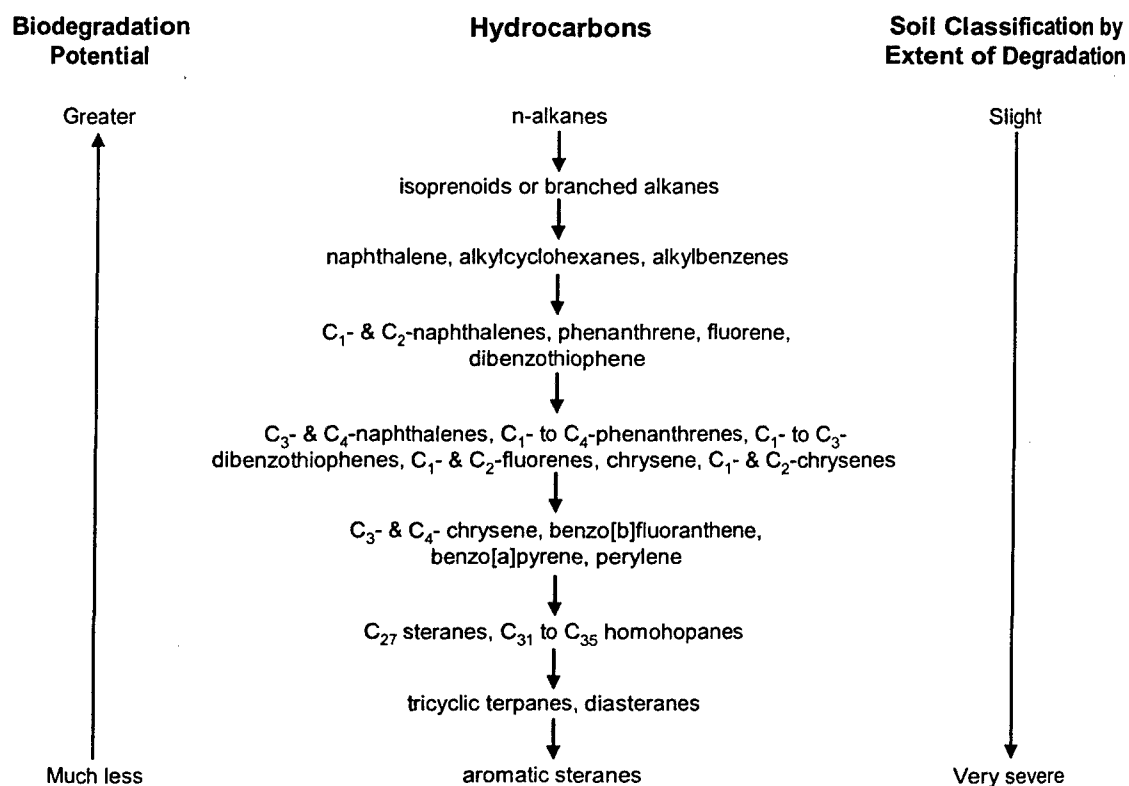


Figure 1. Hierarchy of Biodegradability
(Adapted from Moldowan (1992), as cited in Loehr *et al.* (2001)¹⁵)

This is not to imply that an extraction technique may not be predictive of bioavailability, because that is an open question and requires further investigation. Instead, it seems likely that an exhaustive extraction method cannot be used for biological evaluations because living organisms are not known to have a mechanism to acquire and assimilate all of a compound that is present in soil or sediment, particularly if processes associated with aging have occurred².

The current focus of attention among soil and environmental chemists is not whether external and internal sites for sorption exist but rather the mechanisms of this sorption. For hydrocarbons and other hydrophobic organic compounds, the chief sorbent in soil is its native organic matter. Two mechanisms have been proposed to account for the slow sorption and desorption of nonionic molecules, with the native organic matter in some way serving as the chief sorbent. These mechanisms are commonly termed intraparticle diffusion and intraorganic matter diffusion. The former deals with micropores associated with the inorganic components of the soil, the latter with diffusion within the native organic matter².

According to the intraparticle diffusion model, the solute is within micropores present inside of inorganic particulate matter, but diffusion of the solute is retarded because it is sorbed to the sides of the micropore. These micropore walls are coated with organic matter that rapidly sorbs the hydrophobic solutes. Sorption to the pore walls thus effectively entraps the hydrophobic molecule, retarding its release. Diffusion out of the micropores presumably takes place, but diffusion of a highly hydrophobic molecule will be retarded by (a) the partitioning of the compound between the liquid in the pore and the pore wall and (b) the tortuous path between micropores before reaching the outer surface of the large micropore-filled particle².

Implicit in the intraorganic matter diffusion mechanism are concepts relative to the sorption of hydrophobic compounds by the humic fraction of soil. The compound of concern is considered to be present within the organic matter itself, diffusing both in and out. The humic materials contain extremely small voids or spaces, and the movement of small molecules into and out of these voids is possible. The sizes of these voids, or micropores, are presumably similar to or not much larger than the molecules of concern. Hydrophobic molecules that are sorbed in these pores increase the lipophilicity (the affinity of a molecule for a lipids environment measured in a liquid-liquid system as the log of the octanol-water partition coefficient (K_{ow})) of the microenvironment, thereby further enhancing sorption in these minute pores. As the molecule is traveling over the tortuous intraorganic route, it is repeatedly being sorbed and slowly desorbed. Steric hindrance arises because of pore constrictions and pore walls reducing diffusivity, and it becomes appreciable if the dimensions of the pore are not much greater than those of the hydrophobic molecule².

BIOAVAILABILITY AND SEQUESTRATION OF PETROLEUM HYDROCARBONS IN SOIL

Bioavailability is sometimes considered as synonymous with toxicity to one or another species, sometimes as equivalent to biodegradation by microorganisms, and sometimes as synonymous with uptake or assimilation. A compound may be assimilated and, although toxic, may not cause injury because it is not transported to the tissue, cell or intracellular site where the toxicity can be expressed. A chemical may be taken up into microbial cells but still not be biodegraded because that organism does not contain the requisite catabolic enzymes. Uptake or assimilation is thus a better means of assessing bioavailability, but because of the few studies of uptake per se and the many more of toxicity and biodegradation, the term bioavailability also should be used to include these issues as well².

Considering bioavailability, however, it is obvious that, regardless of which mechanism is more important, the compounds that have undergone slow sorption over a period of time, thus having aged, are deposited in physically remote sites of the soil matrix. For all intents and purposes, they have become sequestered. And in this sequestered state, they may be inaccessible for biodegradation or bioremediation by microorganisms, for uptake by animals or plants and for toxicity to any living organism².

When petroleum hydrocarbons weather in site soils, there are biological (i.e., biodegradation), chemical (e.g., oxidation), and physical (e.g., volatilization and leaching) processes that occur that affect the type of hydrocarbons remaining within the soil matrix over time. For example, as petroleum hydrocarbons weather in site soils, there can be hydrocarbon losses due to volatilization of the lower boiling point fractions (e.g., n-alkanes and BTEX). Losses may also occur from the removal of water-soluble fractions (e.g., low boiling point aromatic hydrocarbons) due to leaching. Petroleum hydrocarbons in soil may also be converted to simpler compounds by microbial processes (i.e., biodegradation) or converted into other compounds via chemical reactions (e.g., oxidation or reduction)¹⁵.

The length of time that petroleum hydrocarbons have been within the soil matrix at a given release site affects the amount of weathering, natural biodegradation and/or sequestration that occurs, depending upon soil type and environmental conditions. However, recent studies indicate that the age of petroleum hydrocarbons in soil does not correlate directly with the duration of weathering or the extent of natural biodegradation that may have occurred. Relatively old (e.g., several decades) petroleum release sites may contain hydrocarbon compounds that have not weathered/biodegraded to any measurable extent. Conversely, relatively recent (e.g., a few months) petroleum release sites may have undergone significant weathering/biodegradation processes¹⁵.

Sequestration of petroleum hydrocarbons in soil results from the binding of these chemical compounds to or within soil particles. The extent of sequestration may be influenced by time, soil organic matter content, clay content, cycles of wetting and drying, chemical type and chemical properties (e.g., water solubility, molecular weight, boiling point). Sequestration has an influence on the extent and rate of biodegradation (i.e., the oxidation of hydrocarbons by microbial processes within the soil matrix). Sequestration can decrease the bioavailability (i.e., availability of a chemical for uptake by organisms, for exerting toxic effects and for biodegradation/bioremediation by microorganisms) of organic compounds to soil organisms, thus reducing toxicity of the contaminated soils¹⁵.

Sequestration and a consequent diminution in bioavailability occur even as a substrate is being biodegraded. If the loss is rapid, the compound will disappear before sufficient time elapses for appreciable sequestration to occur. If the loss rate is slow, the time-dependent sequestration will proceed to render more of the compound unavailable for assimilation or metabolism. However, because soil properties affect the rate and extent of sequestration, it is not presently possible to use loss rate in different soils to predict the amount of a compound that will be sequestered¹⁶. The exposure of humans, animals or plants to a toxicant that is sequestered in soil is less than to the same concentration of the compound that is fully available, and the risk from the compound is consequently less. If the rates and extents of sequestration differ among soils with different properties, it is therefore necessary either to determine the bioavailability of aged compounds in each soil type or to find generalizations allowing a prediction of the effect of soil characteristics on the diminution in bioavailability as a function of time¹⁷.

No clear correlations exist between the toxicity of contaminated soils or soil leachates and the concentration of specific contaminants for either untreated or treated soil samples. This lack of correlation suggests that the total concentration of a contaminant is an inadequate indication of the relative toxicity of a soil².

The lessons learned from the field demonstrations clearly show that simple measures of petroleum hydrocarbon concentrations in soil, such as obtained through TPH analyses, do not

adequately reflect the risk posed to human health or the environment at petroleum release sites. Better measures of petroleum hydrocarbon concentrations in soil, such as those obtained through the application of the TPHCWG approach, or other fractional analysis methodologies, are a step in the right direction. However, even these improved methods cannot measure the amount of petroleum hydrocarbon contaminants that are bioavailable or account for the petroleum hydrocarbons that have become sequestered within the soil matrix.

PETROLEUM HYDROCARBON CLEANUP IN THE UNITED STATES

A summary of the approaches used by the 50 states to evaluate petroleum release sites is shown in Table 3 below. Fractional analyses of TPH and the application of risk-based analyses at sites contaminated with petroleum hydrocarbons are becoming the preferred approaches because these processes lead to more scientifically-based cleanup levels and remedial action decisions. A growing number of states are adopting this approach or are developing variations of the TPHCWG or MADEP methodologies. A state-by-state review also indicates that application of tiered risk assessments at petroleum release sites is rapidly replacing the petroleum hydrocarbon cleanup approach that is solely based upon total TPH concentrations. For example, the Washington State Department of Ecology has evaluated dozens of petroleum release sites under their new cleanup regulation. They have found that, overall, the new process allows responsible parties to take less aggressive cleanup action than would have occurred under the old rules. Under the old rules it was common for cleanup actions to be taken when total TPH concentrations were above 200 mg/kg in site soils. But under the new regulations, that value has risen to more than 2,000 mg/kg at most sites¹⁸.

As indicated in Table 3 below, there are presently eleven states that are using TPH fractions to assess risk at petroleum release sites within the United States. Four of these states (Louisiana, Oregon, Texas and Washington) have adopted the TPHCWG fractions. Five of these states (California, Massachusetts, Montana, North Carolina and South Carolina) have adopted the MADEP fractions. The two remaining states (Alaska and Utah) have adopted slightly different TPH fractions that are variations of the TPHCWG or the MADEP fractions¹⁹. It is also interesting to note that there are significant differences in petroleum fraction toxicity values (reference doses and concentrations) among a few of these states, particularly the states of Massachusetts and Washington. A summary of the TPH fractions and their respective toxicity values that have been adopted by these states and the provisional peer reviewed toxicity values (PPRTV) adopted by the U.S. EPA for Superfund sites is shown in Table 4²⁰.

Table 3: Petroleum Hydrocarbon Cleanup Approaches among the 50 States

State	Cleanup Levels	Risk-based standards	RBCA	BTEX/PAHs as COCs	TPH GRO/DRO	TPH fractions	TPHCWG	MADEP	Other
AK			X	X		X			X
AL	X		X	X	X				
AR			X	X	X				
AZ	X			X					
CA		X		X		X		X	
CO	X								
CT	X			X	X				
DE			X	X	X				
FL		X		X	X				
GA		X	X	X					
HI		X	X	X	X				
IA		X		X					
ID		X	X	X	X				
IL		X	X	X					
IN		X		X					
KS	X			X					
KY		X		X	X				
LA			X	X		X	X		
MA			X	X		X		X	
MD	X			X	X				
ME	X			X	X				
MI		X	X	X	X				
MN	X		X	X					
MO		X		X					
MS	X			X					
MT		X	X	X		X		X	
NC		X	X	X		X		X	
ND	X			X	X				
NE	X		X	X	X				
NH	X			X	X				
NJ	X			X					
NM	X			X					
NV	X				X				
NY	X			X					
OH		X		X	X				
OK									
OR		X	X	X		X	X		
PA	X			X					
RI	X			X	X				
SC		X	X	X		X		X	
SD	X			X					
TN	X			X	X				
TX		X	X	X		X	X		
UT		X	X	X		X			X
VA			X	X					
VT	X			X	X				
WA		X	X	X		X	X		
WI	X			X					
WV	X			X					
WY	X			X					

Table 4: TPH Fraction Toxicity by State⁽¹⁾

TPH Fractions		TPHCWG		Louisiana		Texas		Oregon		Washington	
		RfD	RfC	RfD	RfC	RfD	RfC	RfD	RfC	RfD	RfC
Aliphatic	EC5 - EC6	5.00	5.26	5.00	5.26	5.00	5.26	5.70	5.70	5.70	5.70
	>EC6 - EC8	5.00	5.26	5.00	5.26	5.00	5.26	5.70	5.70	5.70	5.70
	>EC8 - EC10	0.10	0.29	0.10	0.29	0.10	0.29	0.10	0.30	0.03	0.085
	>EC10 - EC12	0.10	0.29	0.10	0.29	0.10	0.29	0.10	0.30	0.03	0.085
	>EC12 - EC16	0.10	0.29	0.10	0.29	0.10	0.29	0.10	0.30	0.03	NA
	>EC16 - EC21	2.00	NA ⁽²⁾	2.00	NA	2.00	NA	2.00	2.00	2.00	NA
	>EC21 - EC35	2.00	NA	2.00	NA	2.00	NA	2.00	2.00	2.00	NA
Aromatic	>EC8 - EC10	0.04	0.06	0.04	0.06	0.04	0.06	0.04	0.06	0.05	0.05
	>EC10 - EC12	0.04	0.06	0.04	0.06	0.04	0.06	0.04	0.06	0.05	0.05
	>EC12 - EC16	0.04	0.06	0.04	0.06	0.04	0.06	0.04	0.06	0.05	NA
	>EC16 - EC21	0.03	NA	0.03	NA	0.03	NA	0.03	0.03	0.03	NA
	>EC21 - EC35	0.03	NA	0.03	NA	0.03	NA	0.03	0.03	0.03	NA
		Alaska		TPH		Massachusetts		TPH		Provisional - U.S.EPA	
Aliphatic		RfD	RfC	fraction	RfD	RfC	fraction	RfD	RfC		
	C6 - C10	5.00	5.26	C5 - C8	0.04	0.03	C5 - C8	0.04	0.03		
	C10 - C25	0.10	0.29	C9 - C18	0.10	0.03	C9 - C18	0.1	0.03		
Aromatic	C25 - C36	2.00	NA	C19 - C32	2.00	NA	C19 - C32	2.0	NA		
	C6 - C10	0.20	0.11	C5 - C8	c.s. ⁽³⁾	c.s.	C5 - C9	c.s.	c.s.		
	C10 - C25	0.04	0.06	C9 - C18	0.03	0.05	C10 - C16	0.02	NA		
	C25 - C36	0.03	NA	C19 - C32	0.03	NA	C17 - C36	0.03	NA		
		Utah									
Aliphatic		RfD	RfC								
	C5 - C6	0.06	0.06								
	C7 - C8	0.06	0.06								
	C9 - C10	0.10	0.29								
	C11 - C12	0.10	0.29								
	C13 - C16	0.10	0.29								
Aromatic	C17 - C21	2.00	NA								
	C22 - C35	2.00	NA								
	C9 - C10	0.04	0.06								
	C11 - C13	0.04	0.06								
	C12 - C22	0.03	NA								

Notes:

(1) - all values are mg/kg-day

(2) - not applicable

(3) - chemical specific

To develop reference doses (RfDs) and reference concentrations (RfCs) for petroleum hydrocarbon fractions, the TPHCWG followed guidance published by the U.S. EPA²¹. The TPHCWG gathered toxicity data for individual compounds, mixtures and whole products that were available at the time (circa 1997). However, the TPHCWG chose not to prioritize use of toxicity data for a single reference compound to represent the health risk of each fraction. Instead, the TPHCWG reviewed all available data applicable to each fraction, prioritizing mixture studies. Using these studies, reasonably conservative RfDs and RfCs were developed for aliphatic and aromatic fractions as determined by the Direct Method. These risk values accounted for the uncertainty in the underlying toxicity data.

Long chain petroleum hydrocarbons, ranging from C₉ to C₁₅, are predominant constituents in weathered jet-fuel spills. To evaluate the potential toxic effects of a C₉ hydrocarbon, *n*-nonane (neat) was administered by repeated oral gavage to groups of 10 female Fischer 344 rats and 10 male C57BL/6 mice at daily doses of 5.0, 1.0, 0.1 and 0 (control) g/kg, 7 days/week for 90 days²². This study was conducted because *n*-nonane is a potential surrogate for the equivalent carbon (EC)₈₋₁₆ aliphatic fraction RfD. Using a no observed adverse effect level (NOAEL) of 0.1 g/kg/day and a minimum uncertainty factor of 1000 (10 for animal to human extrapolation, 10 for sensitive subpopulations and 10 for subchronic to chronic duration of study), the RfD for *n*-nonane would be 0.1 mg/kg/day. This RfD is equal to the current TPHCWG RfD for the EC₈₋₁₆ -

EC₁₆ aliphatic fraction based on an unpublished oral 90-day rat study using a de-aromatized aliphatic mixture of C₉ - C₁₂ alkanes, with application of similar uncertainty adjustments. This study, therefore, would support the current RfD for the fraction should the toxicity value be reassessed²³.

Similarly, a study was conducted using a EC_{>8} - EC₁₆ aromatic fraction prepared from Jet A1 to determine the toxic effects of this fraction as a whole²⁴. Fraction concentrations in corn oil were administered by gavage to groups of 15 female Sprague-Dawley rats and 15 male C57BL/6 mice at daily doses of 500, 100, 20 and 0 mg/kg (vehicle control) for 90 days. At the high dose, lethargy and increased liver weight occurred in both species. Critical effects at the mid-dose included hemoglobin and hematocrit decreases in the female rats. The study NOAEL was 20 mg/kg/day. If the toxicity value is reassessed, this study should be considered as a potential critical study for this fraction. The TPHCWG recognized that new toxicity data were being generated and would continue to be developed on petroleum hydrocarbon compounds and mixtures. Consequently, periodic reviews of petroleum fraction toxicity data were recommended when those data became available²³.

In contrast to the TPHCWG approach, the MADEP chose to use the known toxicity of n-hexane to drive the RfD for their lighter aliphatic fraction (C₅ - C₈). Consequently, the toxicity of this aliphatic fraction is driven by considerations for the potential neurotoxicity (peripheral neuropathy) from exposures to commercial hexanes and potential diketone metabolites of n-alkanes²⁵. As shown in Table 4 above, the RfD adopted by MADEP for the C₅ - C₈ aliphatic fraction is more than two orders of magnitude (0.04 mg/kg-day vs. 5.0 mg/kg-day) below the RfD adopted by the TPHCWG for this fraction.

In developing the PPRTV for petroleum hydrocarbon fractions, the U.S. EPA appears to favor the MADEP approach²⁰. This is particularly true for the light aliphatic fraction (C₅ - C₈) RfD which, as mentioned above, is more than two orders of magnitude lower than the RfD adopted by the TPHCWG for this fraction. Until better toxicity data are available for petroleum hydrocarbon fractions, it appears likely that single component toxicity values, such as the RfD for n-hexane, will drive PPRTV values adopted by the U.S. EPA for use at Superfund sites.

Single component toxicity values may drive cleanup levels unnecessarily low. Hexane toxicity serves as the basis for the MADEP approach and the PPRTV RfD for the C₅ - C₈ aliphatic fraction. Hexane occurs in small quantities in some fuels (e.g., gasoline, JP-4), is not detectable in others (e.g., JP-8, diesel) and is expected, due to its volatility, to have evaporated from weathered fuels spills²⁶⁻²⁷. Therefore, this single component toxicity value used for the entire fraction would likely overestimate risk at a jet fuel spill site.

The state of Oregon has recognized that the toxicity of a specific member of a petroleum hydrocarbon fraction can be much greater than the rest of the members of that fraction. If that component were present as a small part of the total fraction, assigning the toxicity for this component to the entire fraction would overestimate the risk. Consequently, the higher toxicity component is treated separately and the remaining members of the fraction are assigned a more representative toxicity. For the light aliphatic fraction EC₅ - EC₆, n-hexane, the most toxic member of this fraction, is treated separately, and the toxicity of the fraction is based on the toxicity of cyclohexane. Cyclohexane was chosen because this compound appears to be more representative of the other chemicals in this fraction with regard to their toxicity than n-hexane or n-heptane. Consequently, the RfD adopted for this fraction is 5.7 mg/kg-day, as shown in Table 4 above. Other compounds that are treated separately by the state of Oregon include 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene and naphthalene²⁸.

There are clearly significant differences in the RfD for the C₅ - C₈ aliphatic fraction between the TPHCWG and the MADEP methodologies. There is also a very large difference in the RfC for this aliphatic group between the TPHCWG and the MADEP methodologies. A review of the logic behind the choice of critical study(ies) for fraction reference values is periodically needed. Such a review could suggest chronic toxicity studies of fraction-specific surrogate compounds (e.g., *n*-hexane, *n*-heptane, *n*-nonane, eicosane, toluene and pyrene) or representative mixtures. These studies would be needed to refine RfDs and RfCs for aliphatic and aromatic hydrocarbon fractions and ensure consistency among the various fractional analysis methodologies already in use or under consideration.

INTERNATIONAL USERS OF THE TPH FRACTIONAL ANALYSIS APPROACH

The provinces of Nova Scotia, New Brunswick, Prince Edward Island and Newfoundland in Canada have approved use of the RBCA model for the evaluation of human health risks and are considering adoption of the TPH fractional analysis approach developed by the TPHCWG²⁹. Although use of the TPHCWG methodology by other countries is presently unknown, at least one environmental manager who works for an international petroleum distributor successfully used the TPHCWG approach to derive site-specific cleanup goals for a refinery located in Singapore³⁰.

A further review of literature available on the world-wide web indicates that there is considerable international interest in the fractional analysis of petroleum hydrocarbons and the application of the RBCA process using fraction-specific toxicity values at petroleum contaminated sites. For example, the enHealth Council within the Commonwealth of Australia is using the TPHCWG approach to develop an Australian Method for addressing complex TPH mixtures in soil. Presently, health-based investigation levels (HBILs) have been derived for three higher carbon number fractions based on their limited environmental mobility and low volatility. These HBILs are 90 mg/kg for >C₁₆ - C₃₅ aromatics, 5600 mg/kg for >C₁₆ - C₃₅ aliphatics, and 56000 mg/kg for >C₃₅ aliphatics³¹.

It is also evident that natural attenuation or intrinsic bioremediation is receiving considerable international attention as a viable remedial action alternative (under the RBCA process) at petroleum release sites. Intrinsic bioremediation of virgin naphtha at a petroleum release site located in northern Italy and of TPH and BTEX contaminated groundwater at a former petroleum refinery located in the western central region of Germany have successfully demonstrated the utility of natural attenuation as an effective remedial action alternative to the North Atlantic Treaty Organization Committee on Challenges to a Modern Society (NATO/CCMS)³². In fact, the interaction between environmental contaminants, especially for the fate and transport of complex mixtures like petroleum hydrocarbons, is an important subject for further research within the Contaminated Land Rehabilitation Network for Environmental Technologies (CLARINET), a consortium of regulators, industrialists, researchers, scientists, academicians and technology developers from 16 European Countries³³.

Within the United Kingdom, a key research gap for risk-based management of contaminated land includes the need for standardized protocols (such as the TPHCWG methodology) for fingerprinting complex mixtures of petroleum hydrocarbons³⁴. It is also interesting to note that BP Oil Europe developed the Risk-Integrated Software for Cleanups (RISC) package that includes the ability to determine risk-based TPH target levels by incorporating the TPH fractions

proposed by the TPHCWG. With these fractions, the chemical database within RISC contains close to 90 compounds with full physical, chemical and toxicological data³⁵.

FUTURE APPLICATIONS OF TPH FRACTIONAL ANALYSIS METHODS

Most petroleum release sites can and should be evaluated using a risk-based process, such as ASTM's RBCA, supported by TPH fractional analysis methods, such as the approach developed by the TPHCWG. However, before any petroleum release site is evaluated using this methodology, there are several key factors that should be considered.

- The timing of the release is of critical importance. If the release involves fresh product (i.e., a recent spill) that is rapidly absorbed by site soils or is discharged into a receiving body of water (i.e., a stream or lake), carcinogenic components such as benzene are likely to drive human risk.
- If the release is a rapid, one-time event involving a UST or other underground storage or transfer device, emergency response actions taken at the site may be extensive, particularly if the release poses an immediate health and/or safety risk.
- The petroleum release site may include the presence of other contaminants, such as trichloroethylene, that may pose a greater health risk than the petroleum product(s) involved.
- Although the petroleum release may be an old one (i.e., occurred years earlier), the site may not have been previously investigated. Ideally, the nature and extent of the petroleum contamination at a release site should be adequately documented before TPH fractional analysis and RBCA processes are employed.
- The concentrations of TPH in site soils should be above applicable state action levels.
- Natural attenuation of the petroleum product at the release site should be one of the remedies under consideration.

CONCLUSIONS AND RECOMMENDATIONS

The TPHCWG methodology and the MADEP methodology provide similar results. Total TPH concentrations across the TPHCWG and MADEP fractions are likely to compare reasonably well with the total TPH (GRO + DRO). Both approaches provide fractional analysis data and are likely to produce a similar TPH "fingerprint". Both approaches also provide fraction data that can be used in a risk-based framework, such as ASTM RBCA, to assess the risk posed to potential human receptors by petroleum hydrocarbon contamination in site soils. However, the MADEP methodology uses a RfC for the lighter C₅ - C₈ aliphatic fraction that is nearly two orders of magnitude lower than the RfC used by the TPHCWG. Consequently, the MADEP methodology may require more aggressive remedial measures at petroleum release sites, under a given exposure scenario, than remedial measures that would be indicated under the TPHCWG approach. Both approaches are likely to overestimate the actual risk posed to potential human receptors in this exposure scenario because the fate and transport parameters

that are used to calculate Tier 1 RBSLs under ASTM's RBCA process are very conservative. However, as demonstrated at the SANGB site, even those soil samples that contained insufficient TPH concentrations to support fractional analysis by the Direct Method were found to pose a significant risk to potential human receptors when evaluated under the MADEP methodology¹³. Given these results, the MADEP methodology is likely to require more aggressive remedial measures at petroleum release sites than those indicated under the TPHCWG approach.

Fractional analysis of TPH and the application of risk-based analyses at sites contaminated with petroleum hydrocarbons are becoming the preferred approach because the process leads to more scientifically-based cleanup levels and remedial action decisions. A growing number of states and nations are adopting this approach or are developing variations of the TPHCWG or MADEP methodologies. A state-by-state review also indicates that the concept of TPH fractional analysis and the subsequent application of tiered risk assessment at petroleum release sites is rapidly replacing the petroleum hydrocarbon cleanup approach based upon total TPH concentrations alone.

If the total concentration at a polluted site is greater than the regulatory level but the bioavailable concentration is below that value, a site slated for expensive cleanup might, instead, be deemed to present an acceptable risk. The public concern about a contaminated location might be allayed by the more meaningful assessment. Moreover, a site that was bioremediated but still contained concentrations of one or more contaminants above the target levels may have indeed been successfully cleaned up, even though conventional analyses suggested that the remediation was inadequate. This is true both of engineered and intrinsic bioremediation, which frequently do not destroy all of the targeted compounds. Because bioremediation treatments act on the fraction that is bioavailable, to microorganisms at least, the accessibility of the portion that remains may be so low that the site presents little or no risk to higher organisms³⁶.

A critical need for risk-assessments at petroleum release sites is the identification of hydrocarbon and soil properties that affect the availability of TPHs from impacted soils to the environment. Additional insight into the mechanisms that govern the availability of hydrocarbons in soil is also needed. Another critical need for risk-assessments at petroleum release sites is the development of rapid and cost-effective test methods to determine the available hydrocarbons in soil and the rate of release of hydrocarbons from impacted soil to the environment³⁷.

Default values for relative bioavailability of hydrocarbons are used in assessing risks to human health. While a number of such values exist for the dermal exposure pathway, there are few accepted values for oral exposure, and the values that do exist are near unity. The development of widely accepted oral default values for bioavailability would be a valuable contribution towards the cost-effective management of petroleum release sites³⁷.

REFERENCES

1. Loehr, R.C. 2001. Preface. In: Risk-Based Decision-Making for Assessing Petroleum Impacts at Exploration and Production Sites. McMillen, S. J., Magaw, R. I., and Carovillano, R. L., eds. Petroleum Environmental Research Forum and U.S. Department of Energy, Government Printing Office, Washington, D.C.
2. Linz, D. G. and Nakles, D. V. 1997. Environmentally Acceptable Endpoints in Soil Risk-Based Approach to Contaminated Site Management Based on Availability of Chemicals in Soil. American Academy of Environmental Engineers, Annapolis, MD.
3. Weisman, W., ed. 1998. Total Petroleum Hydrocarbon Criteria Working Group Series. Volume 1: Analysis of Petroleum Hydrocarbons in Environmental Media. Amherst Scientific Publishers, Amherst, MA.
4. U.S. EPA. 1989. Risk assessment guidance for Superfund. Volume I: Human health evaluation manual (Part A). Office of Emergency and Remedial Response, U.S. Environmental Protection Agency, Washington, D.C. EPA/540/1-89/002, PB90-155581.
5. ASTM. 1995. Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites, E 1739 – 95. American Society for Testing and Materials, West Conshohocken, PA.
6. Vermulen, E. K., Merrill, E. M., and Sterner, T. R. 1999. TPH Criteria Working Group field demonstration: Misawa Air Base, Japan. Operational Toxicology Branch, Air Force Research Laboratory, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-1999-0029.
7. Merrill, E. A. and Heathman, T. W. 1998. TPH Criteria Working Group Demonstration Field Sampling Report: Marine Corps Air Station, El Toro, CA. Air Force Research Laboratory, Operational Toxicology Branch, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-1999-0028.
8. Heathman, T. W. and Merrill, E. A. 1998. TPH Criteria Working Group Field Demonstration Project: Tinker Air Force Base, OK. Air Force Research Laboratory, Operational Toxicology Branch, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-2001-0187.
9. Merrill, E. M. 1999. TPH Criteria Working Group field demonstration: Scott AFB, Belleville, IL. Operational Toxicology Branch, Air Force Research Laboratory, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-1999-0025.
10. Merrill, E. M. 1999. TPH Criteria Working Group field demonstration: Harrier jet crash site, Fairborn, OH. Operational Toxicology Branch, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-1999-0026.
11. Reed, D. A., Sterner, T. R., and Merrill, E. M. 2001. Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) field demonstration report: Elmendorf Air Force Base, Alaska. Operational Toxicology Branch, Air Force Research Laboratory, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-2001-0118.
12. Reed, D. A. and Sterner, T. R. 2003. Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) Field Demonstration Report: Air Force Plant Number 6 Fuel Farm, Dobbins

AFB, Georgia. Air Force Research Laboratory, Operational Toxicology Branch, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-2002-0158.

13. Reed, D. A., Sterner, T. R., and Sarson, J. 2003. Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) Field Demonstration Report: IRP Site 4, POL Area, Springfield ANG Base, Springfield, Ohio. Air Force Research Laboratory, Operational Toxicology Branch, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-2003-0099.
14. MADEP. 2002. Characterizing risks posed by petroleum contaminated sites: Implementation of the MADEP VPH/EPH approach. Massachusetts Department of Environmental Protection, Boston, MA. Final Policy #WSC-02-411. www.mass.gov/dep/bwsc/vph_eph.htm
15. Loehr, R. C., McMillen, S. J., and Webster, M. T. 2001. Predictions of biotreatability and actual results: Soils with petroleum hydrocarbons. Pract. Period. Hazard. Toxic Radioact. Waste Manag. 5:78-87.
16. Nam, K. and Alexander, M. 2001. Relationship between biodegradation rate and percentage of a compound that becomes sequestered in soil. Soil Biol. Biochem. 33:787-792.
17. Chung, N. and Alexander, M. 1998. Differences in sequestration and bioavailability of organic compounds aged in dissimilar soils. Environ. Sci. Technol. 32:855-860.
18. Kmet, P. 2004. Personal communication: Telephone discussions with Mr. Pete Kmet, P. E., Washington State Department of Ecology, Toxics Cleanup Program, Olympia, WA. 4 February 2004.
19. CleanupLevels.com. Viewed February 2004. Cleanup levels for hazardous waste sites. Links to Internet websites operated by each of the 50 states. www.cleanuplevels.com Updated Sept. 2003.
20. U.S. EPA. 2002. PPRTV derivation support document for total petroleum hydrocarbons. U.S. Environmental Protection Agency, National Center for Environmental Assessment, Superfund Health Risk Technical Support Center, Cincinnati, OH. SRC SF 01-031/10-16-2002. http://hhpptv.ornl.gov/pprtv_papers.shtml
21. U.S. EPA. 1989. Risk assessment guidance for Superfund. Volume I: Human health evaluation manual (Part A). Office of Emergency and Remedial Response, U.S. Environmental Protection Agency, Washington, D.C. EPA/540/1-89/002, PB90-155581.
22. Dodd, D. E., Wolfe, R. E., Pollard, D. L., Merrill, E. A., Sterner, T. R., Bekkedal, M. Y. V., English, J. H., and Weisman, W. H. 2002. 90-Day Oral Toxicity Study on n-Nonane in Female Fischer 344 Rats and Male C57BL/6 Mice. Air Force Research Laboratory, Operational Toxicology Branch, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-2002-0137.
23. Vorhees, D. J., Weisman, W. H., and Gustafson, J. B. 1999. Total Petroleum Hydrocarbon Criteria Working Group. Volume 5: Human health risk-based evaluation of petroleum release sites: Implementing the Working Group Approach. Amherst Scientific Publishers, Amherst, MA.

24. Smith, P. B., Veley, K. E., Yarrington, J. T., Slauter, R. W., and Vorhees, D. 1999. 90-day oral gavage toxicity study of C₉-C₁₆ aromatic fraction of Jet-A in female Sprague-Dawley CD rats and male C57BL/6 mice. Air Force Research Laboratory, Operational Toxicology Branch, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-1999-0229.
25. MADEP. 2003. Updated petroleum hydrocarbon fraction toxicity values for the VPH/EPH/APH methodology. Office of Research and Standards, Massachusetts Department of Environmental Protection, Boston, MA.
26. Potter, T. L. and Simmons, K. E. 1998. Total Petroleum Hydrocarbon Criteria Working Group. Volume 2: Composition of Petroleum Mixtures. Amherst Scientific Publishers, Amherst, MA.
27. Gustafson, J. B., Tell, J. G., and Orem, D. 1997. Total Petroleum Hydrocarbon Criteria Working Group. Volume 3: Selection of Representative TPH Fractions Based on Fate and Transport Considerations. Amherst Scientific Publishers, Amherst, MA.
28. OR DEQ. 2003. Risk-based decision making for the remediation of petroleum-contaminated sites. Oregon Department of Environmental Quality, Land Quality Division, Environmental Cleanup and Tanks Program, Portland, OR.
www.deq.state.or.us/wmc/tank/rbdtm.htm
29. MGI Consultants in Environmental and Earth Sciences. Viewed 15 Oct 2002. Human Health Risk Assessment Services. www.mgi-limited.com
30. Davis, G. 2003. Personal communication: E-mail dated 1/11/03 from Greg Davis, Ph.D., Leader of the Soil and Groundwater Remediation research theme, Environmental Contaminants Research Directorate, Commonwealth Scientific and Industrial Research Organization, Wembley, WA, Australia. Greg.Davis@csiro.au
31. enHealth. 2001. Health-based soil investigation levels. enHealth Council, Commonwealth of Australia, Canberra, ACT, Australia.
www.health.gov.au/pubhlth/publicat/document/metadata/env_soil.htm
32. NATO/CCMS. 1999. NATO/CCMS pilot study: Evaluation of demonstrated and emerging technologies for the treatment and clean up of contaminated land and groundwater (Phase III). 1999 Special session: Monitored natural attenuation. North Atlantic Treaty Organization, Committee on the Challenges of Modern Society. Report # 236. EPA/542/R-99/008. www.epa.gov/tio/download/partner/98annual.pdf
33. Austrian Environment Agency. 2000. 4th Progress Report: CLARINET - Contaminated Land Rehabilitation Network for Environmental Technologies, Reporting period of 1 January to 30 June 2000. Austrian Environmental Agency (Umweltbundesamt), Vienna, Austria. Contract ENV4-CT98-0721. www.clarinet.at
34. Wood, P., Spencer, R., MacNaughton, S. 2002. Audit of Contaminated Land Research in the UK, Final Report. AEA Technology Environment, Harwell, Oxfordshire, England.
www.defra.gov.uk/environment/landliability/pdf/contamland_audit.pdf
35. BP Oil Europe. 1997. Risk-Integrated Software for Cleanups (RISC) users manual. London, UK.

36. Alexander, M. 2000. Aging, bioavailability, and overestimation of risk from environmental pollutants. *Environ. Sci. Technol.* 34:4259-4265.
37. Nakles, D.V., Linz, D.G., McMillen, S., Melton, R., Harju, J., Callow, L., Menzie, C., Alexander, M., Cunningham, S., Saterbak, A., Smith, J., Shatkin, J., Montgomery, C., Parkerton, T., Nicolich, M., Jones, B., McKee, C., Rixey, W., Ghosh, R., Heiger-Bernays, W. 2000. Environmentally Acceptable Endpoints for Hydrocarbon-Contaminated Soils, Final Project Report, Prepared for Gas Research Institute (Contract Number 5094-250-2863) and the Petroleum Environmental Research Forum (Research Area Number 1). ThermoRetec Consulting Corp., Concord, MA.

APPENDIX A

TPHCWG FIELD DEMONSTRATIONS: SUMMARY OF LESSONS LEARNED

**Misawa Air Base, Japan
El Toro Marine Air Station, California
Tinker Air Force Base, Oklahoma
Scott Air Force Base, Illinois
Wright-Patterson Air Force Base, Ohio
Elmendorf Air Force Base, Alaska
Dobbins Air Force Base, Georgia
Springfield Air National Guard Base, Ohio**

MISAWA AIR BASE, JAPAN¹

A total of nine soil samples were obtained within Tank Farm Number 2 at Misawa Air Base, Japan, on 18 and 19 August, 1998 to demonstrate the TPHCWG approach at a known petroleum release site. The samples were all collected at depths ranging from 20 to 31 feet bgs, within the historical zone of contamination established by previous Installation Restoration Program (IRP) investigations. TPH fraction concentrations ranged from less than 100 mg/kg to 2,400 mg/kg. The highest concentrations were detected in the EC₅ - EC₈, EC₈ - EC₁₀ and EC₁₀ - EC₁₂ aliphatic fractions. Only trace quantities of BTEX were detected in the samples. The TPH "fingerprint" obtained from the analytical data was indicative of lightly weathered petroleum product. However, soil sampling constraints made it necessary to group the nine primary soil samples (40 mL each) into three composites to provide sufficient soil volume for laboratory analysis. Consequently, the TPH "fingerprint" was not necessarily representative of TPH contamination across the entire site.

Tier 1 RBSLs calculated for a residential exposure scenario applicable to the site ranged from approximately 3,000 mg/kg for the soil leaching to groundwater pathway to 430,000 mg/kg for the soil volatilization to outdoor air pathway. These results indicated that TPH contamination within the tank farm may have posed unacceptable risk to residential receptors; however, additional soil sampling and analysis was needed to confirm this finding due to the limitations imposed on the soil sampling team (i.e., the low volume of primary soil samples making it necessary to composite samples across boreholes).

Principal lessons learned from this demonstration were as follows:

- Adequate volume (~250 mL) of primary soil samples must be obtained to support the TPHCWG direct method for fractional analysis of petroleum hydrocarbons.
- Primary soil samples should not be combined/composited across boreholes.
- Rapid sample processing is required to minimize the loss of volatiles (e.g., BTEX).
- Site-specific data (e.g., geotechnical) are needed to support RBSL calculations.

EL TORO MARINE AIR STATION, CALIFORNIA²

A total of 15 soil samples were obtained within Site 529 and Site 380A at El Toro Marine Air Station, CA, from 27 August through 4 September 1997 to demonstrate the TPHCWG approach at two former UST sites. Site 529 contained a 25,000-gallon rectangular concrete tank that stored heating oil used to supply a laundry boiler. The tank was removed in June 1997. Site 380A contained a 10,000-gallon UST that stored diesel fuel for an emergency power station. This UST was removed in 1993. Investigations conducted at both sites prior to the demonstration detected TPH above 10,000 mg/kg.

The soil samples obtained from the UST sites were submitted for TPH fractional analysis using the Direct Analytical Method. Companion soil samples, collected end-to-end in 2-inch diameter, 6-inch long brass sleeves, were submitted to a separate laboratory for TPH analysis using conventional methods. The analytical data obtained via conventional methods were consistently two to three times higher in TPH concentrations (mg/kg) than the analytical data obtained via the Direct Method.

RBSLs calculated for Site 529 and Site 380A were higher than California cleanup criteria, with the exception of the RBSL for the soil volatilization to indoor air pathway at Site 529. However, the RBSL calculations were performed by using one-half of the detection limit for non-detected fractions, rendering the calculations highly conservative. Non-detects in the EC₅ - EC₈ aromatic fraction were found to contribute 20% of the risk for the soil volatilization to indoor air pathway.

Principal lessons learned from this demonstration were as follows:

- A detailed sampling and analysis plan should be written and approved prior to conducting field activities at demonstration sites.
- Continuous drilling cores provide very useful lithology. However, previous site investigative data regarding the zone of contamination (vertical and horizontal extent) would significantly reduce drilling requirements.
- Soil samples must be analyzed within prescribed holding times to ensure valid results are obtained.
- TPH analysis by conventional and Direct Methods should be performed by the same analytical laboratory.
- Split samples from the total sample volume should be used for multiple analyses. Use of end-to-end samples obtained from adjacent soil cores is likely to produce significant differences in analytical results.
- Lower detection limits for light-end aliphatic and aromatic hydrocarbons are needed to preclude significant bias in RBSLs.

TINKER AIR FORCE BASE, OKLAHOMA³

Thirteen subsurface soil samples were obtained from UST Site 21, located on Tinker AFB, OK, to demonstrate the TPHCWG approach. Two former 1,000-gallon steel USTs, numbers 286 and 287, used for storage of JP-4 jet fuel and diesel fuel, respectively, were located within Site 21. Both USTs were installed in 1980 and removed in 1994, along with approximately 3,200 ft³ of contaminated soil. A site investigation conducted in 1997 identified TPH contamination ranging from 2,000 to 15,000 mg/kg at depths between 1 and 5.5 feet bgs across the site.

All thirteen soil samples were analyzed for TPH-GRO and TPH-DRO by conventional methods. Seven of the soil samples obtained from Site 21 were analyzed using the Direct Method for hydrocarbon fractionation. TPH-GRO concentrations ranged from 30 to 7,000 mg/kg and TPH-DRO concentrations ranged from 11 to 3,700 mg/kg. The highest concentrations of TPH fractions ranged from 1,100 to 5,100 mg/kg in the EC_{>8} - EC₁₀ and EC_{>10} - EC₁₂ aliphatic fractions. Only trace quantities of BTEX were detected in all samples.

A comparison of conventional TPH analysis data with TPH fractional analysis data indicated that soils with elevated levels of hydrocarbon contamination (i.e., >200 mg/kg) had 18 to 64% higher TPH (GRO + DRO), with an average difference of 44.6%. Soils with contamination levels less than 200 mg/kg TPH (GRO + DRO) typically had non-detectable levels of the hydrocarbon fractions when analyzed by the Direct Method.

Some of the individual samples exceeded their respective RBSLs. Only two samples were slightly above the direct contact RBSLs. Overall, the average TPH levels detected did not exceed the average RBSLs.

Principal lessons learned from this demonstration were as follows:

- For fine grained sandstone layers, continuous coring may be required to collect adequate sample quantities for analyses; however, the method of choice is the split spoon to avoid heating of the soil during sampling.
- Soil contaminant levels of at least 200 ppm TPH are needed for useful results from the Direct Method analyses.
- Results at Tinker AFB Site 21 using the Direct Method correlate well with results from conventional TPH and BTEX analyses.
- Fate and transport equations used in the RBCA risk analysis cannot predict the TPH concentrations found in the groundwater and soils at this site. The levels calculated by the equations are too conservative.
- The average RBSLs calculated using the Working Group approach indicate that present levels of TPH contamination are not a hazard to human health and the environment.

SCOTT AIR FORCE BASE, ILLINOIS⁴

Eight soil samples were collected in May 1998 for this TPHCWG demonstration. Samples were taken at approximately 8 to 9 feet bgs within stained areas on the excavation walls of a former UST site on Scott AFB, IL. The open excavation was the former site of two 50,000-gallon USTs used to store JP-8 jet fuel. At the time of their removal, both USTs were in excellent condition with no evidence of leakage. The soil staining that was evident around and beneath the USTs was believed to have resulted from tank piping leaks, overfills or spills within the area of the UST beds. Over 800 cubic yards of soil were removed during the excavation of the USTs in May 1997.

Only two of the eight soil samples contained sufficient TPH concentrations to provide detectable levels across the TPH aliphatic and aromatic fractions. Approximately 13 to 21% of the aliphatic hydrocarbons detected were in the $EC_{>8}$ to EC_{10} range, 26 to 31% were in the $EC_{>10}$ to EC_{12} range and 20 to 22% were in the $EC_{>12}$ to EC_{16} range. Less than 8% of the TPH was detected in the aromatic $EC_{>12}$ to EC_{16} range. Evaporative weathering was demonstrated by the lack of light hydrocarbons in the aliphatic and aromatic fractions. Biodegradation was indicated by the loss of n-alkanes. Highly branched alkanes predominated. These compounds are generally resistant to biodegradation and compose the majority of the JP-8 fuel.

Seven of the eight soil samples contained detectable levels of TPH-GRO and TPH-DRO, with concentrations ranging from 18 mg/kg to (GRO+DRO) to over 1,700 mg/kg (GRO+DRO). The two soil samples with the highest TPH concentrations contained 1,710 mg/kg (GRO+DRO) and 500 mg/kg (GRO+DRO). Total TPH concentrations detected by the Direct Method were 598 mg/kg and 281 mg/kg, respectively. The analytical laboratory reported that it was difficult to obtain a homogeneous aliquot from the soil samples, which probably accounted for some of the large difference in total TPH detected between the Direct Method and conventional method (Method 8015B) analyses. In addition, because JP-8 is a middle distillate, it spans both the GRO and DRO ranges. Consequently, Method 8015B DRO and American Petroleum Institute (API) method for GRO combined could result in some overlap and overestimation of TPH concentrations.

The highest TPH fractions detected in site soils did not exceed the RBSLs for all pathways evaluated (under both a residential and commercial exposure scenario), with the exception of

the subsurface soil volatilization to indoor air pathway RBSLs (115 mg/kg and 303 mg/kg, respectively). This pathway was evaluated as a potential future exposure pathway for the demonstration; however, the pathway was incomplete and unlikely to ever apply to the site. The most restrictive RBSL for the other exposure pathways evaluated was 3,924 mg/kg (using one-half the detection limit for non-detects) for the residential direct contact pathway. None of the TPH concentrations in site soils exceeded this RBSL. Based upon these RBSL calculations, exposure risks were considered acceptable and site closure was recommended.

Principal lessons learned from this demonstration were as follows:

- The higher TPH concentrations detected in site soils using conventional analyses (API method GRO and Method 8015B DRO) vs. Direct Method fractional analysis may be attributable to soil matrix effects (the soil sampled was a highly compacted silty clay with high moisture content that was not easily homogenized).
- Conventional analysis extraction using methylene chloride may be more efficient than Direct Method extraction using n-pentane.
- Direct Method analysis results in non-detects for both aliphatic and aromatic fractions when total TPH concentrations are less than 200 mg/kg in site soils.
- Evaporative weathering of the TPH contamination detected in site soils was demonstrated by the lack of light hydrocarbons (i.e., EC₅ to EC₈).
- Biodegradation was indicated by the loss of n-alkanes.
- The TPHCWG approach provides a better understanding of TPH contamination at petroleum release sites (i.e., it provides a TPH "fingerprint").
- Where TPH profiles (i.e., the TPH "fingerprint") are similar across a petroleum release site, less expensive conventional analysis may be used to assess the extent of contamination. In these situations, only a few samples need to be analyzed using the Direct Method to calculate RBSLs and assess human health risk using the RBCA process.

WRIGHT-PATTERSON AIR FORCE BASE, OHIO⁵

Six subsurface (1 to 2 feet bgs) soil samples were collected within a Harrier Jet impact area approximately two weeks after the crash to demonstrate the TPHCWG approach. The crash occurred on 16 October 1997 near Wright-Patterson AFB, OH. The impact area (approximately 21 feet wide by 55 feet long) was estimated to contain approximately 3,200 kilograms of JP-8 jet fuel. The six soil samples were obtained from the same locations sampled the previous day to assess the degree of contamination and cleanup requirements. Scheduling and site restriction problems precluded the simultaneous collection of samples that could have been split on site for comparison of Direct Method and conventional TPH analysis results.

TPH concentrations detected in site soils collected within the impact area ranged from 3,100 mg/kg to 8,500 mg/kg using conventional analytical methods. Total TPH concentrations detected using the Direct Method of analysis ranged from 389 mg/kg to 11,657 mg/kg. BTEX and carcinogenic PAHs were either not detected or were detected at concentrations that did not exceed regulatory limits. Across all samples, the average TPH concentration detected by conventional analytical methods was 7,067 mg/kg and the average total TPH concentration detected using the Direct Method of analysis was 5,493 mg/kg. Although the average TPH concentration in site soils was very similar between conventional and Direct Method analysis data, the conventional method detected higher levels of TPH in most samples.

All soil samples analyzed by the Direct Method contained similar profiles of hydrocarbons in the $EC_{>8}$ - EC_{10} , $EC_{>10}$ - EC_{12} and $EC_{>12}$ - EC_{16} aliphatic fractions. Over 45% (by weight) of the TPH was detected in the $EC_{>10}$ - EC_{12} aliphatic fraction. The weight percentage of TPH in the aromatic fractions was below 15%. The TPH "fingerprint" indicated by the Direct Method results was fairly consistent with JP-8 fuel; however, some degree of photolysis and microbial degradation was indicated by the lack of n-alkanes and highly branched alkanes.

RBSLs calculated for a residential exposure scenario were lowest for the soil leaching to groundwater pathway. RBSLs for this pathway ranged from 3,125 to 4,410 mg/kg. Higher RBSLs, calculated for the direct contact pathway, ranged from 5,709 to 6,780 mg/kg. However, for a commercial exposure scenario, RBSLs for the direct contact pathway were consistently lower than other exposure pathways that were evaluated. Overall, TPH RBSLs calculated for the residential exposure scenario were 4 to 7 times higher than the Ohio action level for residential land use. TPH RBSLs calculated for the commercial exposure scenario were 11 to 23 times higher than Ohio Category 3 action levels. Under current and future land uses for the impacted area, TPH RBSLs calculated for the commercial exposure scenario were applicable to the site. These RBSLs were found to be 8 to 18 times higher than the Ohio emergency action level (Category 4) of 1,156 mg/kg.

Principal lessons learned from this demonstration were as follows:

- TPH concentrations detected in site soils using conventional analysis methods were consistently higher than the total TPH concentrations detected using the Direct Method.
- The TPH "fingerprint" obtained from the Direct Method analysis of site soils was characteristic of JP-8 fuel that had been subjected to some photo- and biodegradation.
- BTEX and carcinogenic PAHs concentrations did not exceed regulatory limits. Consequently, site cleanup requirements were driven by non-carcinogenic aliphatic and aromatic hydrocarbon concentrations in site soils.
- TPH RBSLs calculated for a residential and commercial exposure scenario were approximately 4 and 11 times higher, respectively, than TPH cleanup criteria determined using the Category 3 levels indicated by the Ohio EPA Guidance for Emergency Response.

ELMENDORF AIR FORCE BASE, ALASKA⁶

Ten soil samples were collected in September 2000 at a former UST site at Elmendorf AFB, AK, to demonstrate the TPHCWG approach. The UST, a 1,200-gallon single-walled tank used to store diesel fuel to heat a recreational cabin, was removed in July 1997. The tank was found to be in good condition with slight rust but no visible holes. The surrounding soil, however, contained TPH contamination in excess of 1,000 mg/kg. Although the source of the petroleum hydrocarbon contamination was not determined, it was believed to be the result of leaks in the transfer piping and/or from overfilling activities.

All soil samples were analyzed for BTEX, carcinogenic PAHs, TPH-GRO, TPH-DRO and TPH fractions by the same analytical laboratory. No benzene or toluene was detected above method detection limits. Ethylbenzene was detected at a maximum concentration of 870 µg/kg and xylenes were detected at a maximum concentration of 4,400 µg/kg. Naphthalene was the only PAH detected at a maximum concentration of 1,700 µg/kg. TPH-GRO concentrations ranged from 1 to 520 mg/kg and TPH-DRO concentrations ranged from 7 to 1,200 mg/kg. Six of the ten soil samples contained TPH-DRO at concentrations above the Alaska Department of

Environmental Conservation Method Two cleanup standard (250 mg/kg) for petroleum migration to groundwater.

Field screening data obtained using a PID correlated well with the TPH concentrations detected in all but one of the soil samples. In addition, in all soil samples that contained detectable levels of TPH, petroleum fractional analysis data indicated very good consistency between the aliphatic and aromatic weight fractions and the respective TPH-GRO and TPH-DRO concentrations. The TPH "fingerprint" also indicated that the petroleum contamination detected in site soils came from a single source (i.e., the former diesel fuel UST).

RBSLs calculated using both recreational and commercial exposure scenarios indicated that the subsurface soil indoor vapor inhalation pathway consistently contained the lowest values, ranging from 955 mg/kg to 10,900 mg/kg. For this pathway, one of the ten samples contained a total TPH concentration above the Tier 1 RBSL for the recreational exposure scenario. Much of the risk was attributable to the $EC_{>8}$ - EC_{10} aliphatic fraction. Under the commercial exposure scenario, four of the ten soil samples contained TPH at concentrations above the Tier 1 RBSL for this pathway. Most of the risk was attributable to the $EC_{>8}$ - EC_{10} and $EC_{>10}$ - EC_{12} aliphatic fractions.

Principal lessons learned from this demonstration were as follows:

- Field screening of soil samples with a PID generally provides a good indication of the level of petroleum hydrocarbon contamination and can greatly aid the field team in selecting sampling intervals where TPH concentrations are likely to be at their maximum values.
- TPH-GRO and TPH-DRO concentrations in site soils should correlate relatively well with total TPH aliphatic and aromatic fractions when the analysis is performed on split samples by the same analytical laboratory.
- A first order "fingerprint" analysis can provide good insight into the consistency of TPH profiles at a petroleum release site.
- Tier 1 TPH RBSLs calculated for the TPHCWG aliphatic and aromatic fractions using appropriate exposure scenarios provide a more scientific basis for remedial action decisions at petroleum release sites than cleanup standards that are based upon TPH-GRO and TPH-DRO concentrations obtained using conventional analytical methods.

DOBBINS AIR FORCE BASE, GEORGIA⁷

A total of 15 soil samples were collected at a former above ground storage fuel farm contaminated with "weathered" jet fuel (JP-4, JP-5 and JP-8) to demonstrate the TPHCWG approach. Located at Air Force Plant Number 6, Dobbins AFB, GA, the fuel farm was operated from the mid- 1950s through the early 1990s. It served as an aircraft fuel storage facility for JP-4, JP-5 and JP-8 fuels. The facility is approximately 300 feet in width and some 500 feet long. It contains eight 50,000-gallon above ground storage tanks. The fuel farm was abandoned in 1993.

All soil samples used for this demonstration were split samples obtained from residual soil core volumes collected by the principal on-site contractor. All BTEX, carcinogenic PAHs, TPH-GRO and TPH-DRO analyses was performed by the on-site contractor's analytical laboratory. TPH fractional analysis by the Direct Method was performed by OpTech's analytical laboratory on the separate, split sample soil volumes.

BTEX was detected above method detection limits in most of the samples. Benzene concentrations ranged from 1300 µg/kg to 31,000 µg/kg. Toluene concentrations ranged from 230 µg/kg to 31,000 µg/kg, ethylbenzene from 1,700 µg/kg to 33,000 µg/kg, and xylenes from 1520 µg/kg to 92,000 µg/kg. Some PAHs were also detected in the samples with elevated BTEX levels. Naphthalene concentrations ranged from 2,900 µg/kg to 23,000 µg/kg. Some fluorene, phenanthrene and fluoranthrene were also detected in samples with elevated BTEX concentrations. No other PAHs were detected above method detection limits in any of the other samples. TPH-GRO concentrations ranged from less than 1 mg/kg to 3,400 mg/kg. TPH-DRO concentrations ranged from 7.8 mg/kg to 9,800 mg/kg.

The highest concentrations of petroleum hydrocarbons were detected in the EC_{>12} - EC₁₆ aliphatic fraction. This result is consistent with the TPH-DRO analytical data, which indicate that much of the detectable TPH was in the DRO range. The sum of the petroleum fraction concentrations, however, is significantly less than the sum of the TPH-GRO and DRO concentrations for those samples containing detectable levels of petroleum hydrocarbons. Measured concentrations of TPH fractions (i.e., with all non-detects set to one-half the detection limit) ranged from 42.9 percent to 89.8 percent of the total TPH (GRO + DRO), with an overall average of 67 percent for the five samples containing detectable TPH concentrations. Although better agreement between total TPH and TPH fraction concentrations was anticipated, the differences are probably attributable more to the sample collection methodology than to differences between the analytical laboratories. TPH-GRO and BTEX concentrations were measured using sealed soil core segment samplers. The TPH-DRO, PAH and TPH fraction concentrations were then measured from the remaining soil.

Flame ionization detector (FID) readings correlated poorly with the concentration of petroleum hydrocarbons in site soils. Although three of the five samples that contained high concentrations of petroleum hydrocarbons also had high FID readings, four of the twelve samples with lower concentrations of petroleum hydrocarbons also had high FID readings. Daily calibrations with methane and functional tests of the FID indicated that the instrument was operating properly. Consequently, the poor agreement between FID readings and petroleum hydrocarbon concentrations in site soils is believed to be attributable to the presence of hydrocarbon vapors in the ambient air during sampling activities. Frequent aircraft operations in the vicinity (i.e., on the nearby taxiways and runway) were noted by the field sampling team while their soil coring/sampling activities were in progress.

A first order "fingerprint" analysis indicated that for all five samples with detectable levels of petroleum compounds, the weight percent of aliphatic fractions ranged from 80.66% to 88.67%. The weight percent of aromatic fractions ranged from 11.33% to 19.34%. Further analysis indicated generally good agreement between the weight fractions of the heavier aliphatic and aromatic hydrocarbons and the weight percent of DRO (83.48% vs. 75.68%, respectively). However, agreement between the weight fractions of the lighter aliphatic and aromatic hydrocarbons and the weight percent of GRO was poor (6.27% vs. 24.3%, respectively). It is evident from this analysis that the petroleum contamination detected in site soils at the fuel farm is inconsistent with the weathered fuel "fingerprint" (i.e., low concentrations of TPH-GRO and little or no BTEX) that was expected at a facility that has been inactive for more than eight years.

Tier 1 RBSLs calculated for a commercial/industrial exposure scenario indicated that the subsurface soil indoor vapor inhalation pathway consistently contained the lowest total TPH

RBSLs, ranging from 99 mg/kg to 359 mg/kg. For this pathway all five samples with detectable concentrations of TPH fractions exceeded their respective total TPH RBSLs. Much of the risk was due to the high concentrations of TPH in the EC_{>8} - EC₁₀, EC_{>10} - EC₁₂ and EC_{>12} - EC₁₆ aliphatic fractions. However, the risk was also attributable to the high concentrations of TPH in the EC₅ - EC₇ (benzene) and the EC_{>10} - EC₁₂ aromatic fractions. Total TPH RBSLs calculated for the subsurface soil to outdoor vapor inhalation pathway ranged from 62,500 mg/kg to 967,000 mg/kg. None of the five soil samples that contained detectable levels of petroleum contamination exceeded their respective total TPH RBSLs for this pathway. It is evident from this dual pathway analysis that the high concentrations of aromatic hydrocarbons in the lighter fractions are driving the risk posed by the petroleum contamination in fuel farm soils.

Principal lessons learned from this demonstration were as follows:

- The same soil samples should be used (preferably by the same laboratory) to obtain total TPH, TPH-GRO, TPH-DRO, BTEX and TPH fractional analysis data. Comparisons between TPH-GRO, TPH-DRO and TPH fractional analysis data cannot be made when different soil sample sets are used for laboratory analysis.
- Ambient temperature headspace (ATH) FID or PID readings should be used to identify soil samples likely to contain the highest concentrations of TPH. Open air FID or PID readings of soil samples are likely to be misleading. This is particularly true when fuel vapors may be present in the ambient air.
- Petroleum release sites containing relatively high concentrations of TPH-GRO and BTEX are inappropriate/unsuitable for demonstration of the TPHCWG methodology.
- Candidate sites for demonstration of the TPHCWG approach should be located in states that apply cleanup criteria based upon TPH concentrations (i.e., TPH-GRO and TPH-DRO) or upon TPH concentrations in the TPHCWG aliphatic and aromatic fractions.

SPRINGFIELD AIR NATIONAL GUARD BASE, OHIO⁸

The IRP Site 4, Petroleum, Oils and Lubricants (POL) Area at Springfield Air National Guard Base, OH, was selected for a field demonstration of the TPHCWG methodology because at least one major fuel spill was known to have occurred at the site. In addition, previous site investigations had detected TPH at concentrations above 1,000 mg/kg. The site also offered an opportunity to evaluate both the TPHCWG and the MADEP methodologies using analytical data obtained from the same sample set.

A total of ten subsurface soil samples were obtained from this demonstration site. The maximum soil sampling depth was 6 feet bgs. Soil samples were selected for laboratory analysis based upon portable PID readings of sample cores. A background sample in an area known to be upgradient of the petroleum contamination was also obtained for laboratory analysis. The soil samples were shipped to Lancaster Laboratories, Lancaster, PA, for TPH fractional analysis using the TPHCWG approach and the MADEP methodology.

No benzene and only trace concentrations of toluene, ethylbenzene and xylenes were detected in any of the samples collected from the site. Only two PAHs (naphthalene and 2-methylnaphthalene) were detected above method detection limits. TPH-GRO and TPH-DRO were detected in all primary soil samples. TPH-GRO concentrations ranged from 9.1 mg/kg to 270 mg/kg. TPH-DRO concentrations ranged from 22 mg/kg to 360 mg/kg. The highest concentration of TPH (GRO + DRO) was 560 mg/kg. Eight of the ten soil samples contained

sufficient TPH to support fractional analysis by the Direct Method. Most of the TPH that was detected was aliphatic hydrocarbons in the $EC_{>8} - EC_{10}$ and $EC_{>10} - EC_{12}$ fractions. Very low concentrations of light aliphatic hydrocarbons and only trace concentrations of light aromatic hydrocarbons were detected. The aliphatic and aromatic fractions detected using the MADEP analytical methodology also indicated that the TPH in SANGB POL area soils was predominately composed of aliphatic hydrocarbons in the $EC_{>10} - EC_{12}$ fraction. No aliphatic hydrocarbons were detected in the $EC_{>16} - EC_{21}$ and $EC_{>21} - EC_{35}$ fractions; only a few samples were found to contain any aromatic hydrocarbons in the $EC_{>10} - EC_{12}$ and $EC_{>12} - EC_{16}$ fractions. These results, in combination with the finding of very low concentrations of BTEX, indicated that the TPH detected in site soils was composed of a weathered petroleum mixture.

The TPHCWG fractional analysis results tended to underestimate the total TPH (GRO + DRO) detected in site soils and the MADEP fractional analysis results tended to overestimate total TPH. The underestimation of TPH using the Working Group methodology and the overestimation of TPH using the MADEP methodology was particularly evident in two of the ten soil samples. Most of the overestimation by the MADEP methodology was attributable to "double addition" resulting from the overlap between the $C_9 - C_{12}$ (VPH) aliphatic fraction and the $C_9 - C_{18}$ (EPH) aliphatic fraction. Most of the underestimation by the TPHCWG methodology was attributed to poor recoveries of petroleum hydrocarbons from the soil matrix.

Field screening data obtained with a portable PID were collected immediately above the soil cores. With the exception of the PID readings obtained for two of the ten samples, there was generally good agreement between the field screening results and the total TPH (GRO + DRO). There was also relatively good agreement between the petroleum odor noted by the sampling team and the PID readings.

A first order "fingerprint" analysis was performed using the five samples that contained the highest concentrations of TPH (GRO + DRO). The weight percent of aliphatic fractions ranged from 74.05% to 83.92% using the TPHCWG methodology, and from 77.8% to 81.3% using the MADEP methodology. The weight percent of aromatic fractions ranged from 16.08% to 25.95% and from 18.7% to 22.2%, using the TPHCWG and using the MADEP methodologies, respectively. The average weight fractions of the heavier aliphatic and aromatic hydrocarbons was 65.98% for the TPHCWG fractions and 63.34% for the MADEP fractions compared to an average weight percent of 55.3% for DRO. There was also good agreement between the average weight fractions of the lighter aliphatic and aromatic hydrocarbons and the average weight percent of GRO (33.90% vs. 44.7% for the TPHCWG fractions and 36.6% vs. 44.7% for the MADEP fractions).

The subsurface soil indoor vapor inhalation pathway consistently contained the lowest total TPH RBSLs. For this pathway all ten samples exceeded their respective total TPH RBSLs, using the MADEP fractions, and seven of the ten samples exceeded their respective total TPH RBSLs, using the TPHCWG fractions. For the subsurface soil outdoor vapor inhalation pathway, none of the samples analyzed for the TPHCWG fractions contained TPH at a concentration that exceeded any of the fraction-specific RBSLs. However, five of the ten samples analyzed for the MADEP fractions exceeded the fraction-specific RBSL for the $C_5 - C_8$ aliphatic fraction. This significant difference in risk was expected because the MADEP RfC for this fraction is nearly two orders of magnitude lower than the TPHCWG RfC (0.2 mg/m^3 vs. 18.4 mg/m^3).

Total TPH concentrations across the TPHCWG and MADEP fractions compared reasonably well with the total TPH (GRO + DRO), although the MADEP methodology appeared to overestimate TPH concentrations to a greater extent than the TPHCWG approach.

underestimated the TPH concentrations in site soils. Both approaches provided fractional analysis data that gave essentially the same TPH "fingerprint". Both approaches yielded data that could be used within the RBCA framework to assess the risk posed to potential human receptors by petroleum hydrocarbon contamination in site soils. However, the TPHCWG approach provided better insight into the nature of petroleum hydrocarbon contamination (i.e., it provided more robust fractional analysis data) and was less likely to overestimate the risk posed to human receptors under the same exposure scenario.

Principal lessons learned from this demonstration were as follows:

- The TPHCWG approach is likely to underestimate the total TPH in site soils due to poor recoveries of petroleum hydrocarbons from the soil matrix.
- The TPHCWG Direct Method does not provide useful fractional analysis data when TPH concentrations in site soils are less than 100 mg/kg.
- The MADEP methodology tends to overestimate the total TPH in site soils primarily because of the analytical overlap between the $C_9 - C_{12}$ (VPH) aliphatic fraction and the $C_9 - C_{18}$ (EPH) aliphatic fraction.
- Portable PID readings generally provide a good indication of the relative concentrations of TPH in subsurface soil core samples.
- The TPH "fingerprint" obtained from MADEP fractional analysis data compares very well to the TPH "fingerprint" obtained from TPHCWG fractional analysis data when the laboratory analysis is performed on the same set of soil samples.
- Under the same exposure scenario, the calculated risk to potential human receptors at petroleum release sites is likely to be higher using the MADEP methodology than it is using the TPHCWG methodology.

REFERENCES

1. Vermulen, E. K., Merrill, E. M., and Sterner, T. R. 1999. TPH Criteria Working Group field demonstration: Misawa Air Base, Japan. Operational Toxicology Branch, Air Force Research Laboratory, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-1999-0029.
2. Merrill, E. A. and Heathman, T. W. 1998. TPH Criteria Working Group Demonstration Field Sampling Report: Marine Corps Air Station, El Toro, CA. Air Force Research Laboratory, Operational Toxicology Branch, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-1999-0028.
3. Heathman, T. W. and Merrill, E. A. 1998. TPH Criteria Working Group Field Demonstration Project: Tinker Air Force Base, OK. Air Force Research Laboratory, Operational Toxicology Branch, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-2001-0187.
4. Merrill, E. M. 1999. TPH Criteria Working Group field demonstration: Scott AFB, Belleville, IL. Operational Toxicology Branch, Air Force Research Laboratory, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-1999-0025.
5. Merrill, E. M. 1999. TPH Criteria Working Group field demonstration: Harrier jet crash site, Fairborn, OH. Operational Toxicology Branch, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-1999-0026.
6. Reed, D. A., Sterner, T. R., and Merrill, E. M. 2001. Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) field demonstration report: Elmendorf Air Force Base, Alaska. Operational Toxicology Branch, Air Force Research Laboratory, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-2001-0118.
7. Reed, D. A. and Sterner, T. R. 2003. Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) Field Demonstration Report: Air Force Plant Number 6 Fuel Farm, Dobbins AFB, Georgia. Air Force Research Laboratory, Operational Toxicology Branch, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-2002-0158.
8. Reed, D. A., Sterner, T. R., and Sarson, J. 2003. Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) Field Demonstration Report: IRP Site 4, POL Area, Springfield ANG Base, Springfield, Ohio. Air Force Research Laboratory, Operational Toxicology Branch, Wright-Patterson AFB, OH. AFRL-HE-WP-TR-2003-0099.

APPENDIX B

TPHCWG AND MADEP METHODOLOGIES

The Total Petroleum Hydrocarbon Criteria Working Group TPH fractions were identified through an analysis of physical-chemical properties (e.g., molecular weight, boiling point, vapor pressure and water solubility) of subsets of complex hydrocarbon mixtures (called fractions) that behave similarly in environmental media. The aliphatic hydrocarbons with similar fate and transport characteristics were grouped into the following fractions based on effective carbon number: $EC_5 - EC_6$, $EC_{>6} - EC_8$, $EC_{>8} - EC_{10}$, $EC_{>10} - EC_{12}$, $EC_{>12} - EC_{16}$, $EC_{>16} - EC_{21}$ and $EC_{>21} - EC_{35}$. Similarly, the aromatic hydrocarbons with similar fate and transport characteristics were grouped into the fractions: $EC_{>6} - EC_8$, $EC_{>8} - EC_{10}$, $EC_{>10} - EC_{12}$, $EC_{>12} - EC_{16}$ and $EC_{>16} - EC_{21}$. Aliphatic and aromatic volatile and semi-volatile hydrocarbons are detected in site soils using the Direct Analytical Method developed by the TPHCWG with assistance from the Shell Development Company^{1,2}.

The MADEP based its TPH fractions on chemical structure, carbon number and structure activity relationships. The MADEP aliphatic fractions include $C_5 - C_8$, $C_9 - C_{18}$ and $C_{19} - C_{36}$ carbon ranges. The MADEP aromatic fractions include the $C_9 - C_{10}$ and $C_{11} - C_{22}$ carbon ranges. The aromatic $C_6 - C_8$ compounds are evaluated individually. The MADEP uses two distinct analytical protocols to analyze petroleum hydrocarbons in water and soil: (1) the volatile petroleum hydrocarbons (VPH) protocol for light aliphatic and aromatic fractions; and (2) the extractable petroleum hydrocarbons (EPH) protocol for the medium to heavy aliphatic and aromatic fractions³.

Both the TPHCWG and MADEP analytical protocols for the volatile-range aliphatic and aromatic hydrocarbons use purge and trap GC with FID and PID detectors in series. However, the MADEP protocol requires methanol preservation of the sample in the field and starts with the retention time at the end of n-pentane due to the difficulty in fully resolving pentane from the methanol solvent peak in soils. Under the TPHCWG protocol, calibration of $EC_{<5}$ through EC_6 aliphatics is determined based on the response of 2-methylpentane and $EC_{>6}$ through EC_8 aliphatics are based on n-heptane response. The MADEP method defines the calibration ranges differently (EC_5 through EC_8) and uses the average response for n-pentane, 2-methylpentane and 2,2,4-trimethylpentane^{1,3}.

Semi-volatile aliphatic and aromatic hydrocarbons are extracted from soil using n-pentane under the TPHCWG method and methylene chloride under the MADEP method. Both methods provide similar results for extractable range hydrocarbons; however, the MADEP method sometimes gives lower values in the $C_9 - C_{12}$ range because more sample handling is required in the laboratory. On the other hand, when the petroleum contamination in the soil is heavyweight motor oil, crude oil or bunker C, the MADEP method is more likely to provide a better measure of petroleum hydrocarbons in the $C_{17} - C_{32}$ range. The MADEP method also appears to more accurately measure extractable petroleum hydrocarbons when moisture content in the soil is relatively high (e.g., > 30%)⁴. As mentioned previously, both the TPHCWG and MADEP methodologies provide TPH fractional analysis data that can be used within the RBCA framework to assess risk at petroleum release sites.

The RBCA process recognizes that chemical release sites vary greatly in their complexity, physical and chemical characteristics, and in the risk they may pose to human and ecological receptors. Consequently, the RBCA process integrates site assessment and response actions with human health and ecological risk assessment to determine the need for remedial action and to tailor corrective action activities to site-specific conditions and risks. The evaluations and methods used in the RBCA process begin with a Tier 1 analysis that uses a "generic" approach and moves through more complex evaluations in either Tier 2 or Tier 3, as needed, based upon site-specific conditions. The ASTM RBCA guide for petroleum release sites (ASTM E 1739-95)

was published in 1995⁵. This RBCA guidance document was adopted by the TPHCWG and MADEP and was used to calculate RBSLs for residential and commercial exposure scenarios at the TPHCWG field demonstrations sites discussed in this report.

REFERENCES

1. Weisman, W., ed. 1998. Total Petroleum Hydrocarbon Criteria Working Group Series. Volume 1: Analysis of Petroleum Hydrocarbons in Environmental Media. Amherst Scientific Publishers, Amherst, MA.
2. Rhodes, I.A. 1998. Characterization of C6 to C35 petroleum hydrocarbons in environmental samples: total petroleum hydrocarbons, aliphatic hydrocarbons, aromatic hydrocarbons, approximate boiling point/carbon number distribution. Method available online from Association for Environmental Health and Sciences. Site viewed 7 July 2004. <http://www.aehs.com/publications/catalog/tph.htm>
3. MADEP and ABB Environmental Services, Inc. 1994. Interim final petroleum report: Development of health-based alternative to the total petroleum hydrocarbon (TPH) parameter", Prepared for Bureau of Waste Site Cleanup, MADEP. Office of Research and Standards, Massachusetts Department of Environmental Protection, Boston, MA. ABB Environmental Services, Inc, Wakefield, MA. www.mass.gov/dep/bwsc/vph_eph.htm
4. Entz, R. 2002. Personal communication: Telephone conversation on 10 October, 2002 with Mr. Richard Entz, Environmental Principal Specialist, Lancaster Laboratories, Lancaster, PA.
5. ASTM. 1995. Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites, E 1739 – 95. American Society for Testing and Materials, West Conshohocken, PA.

APPENDIX C

GLOSSARY OF TERMS

GLOSSARY OF TERMS

Aging: Aging relates to the length of time that hydrocarbons have been in soil and subject to natural environmental conditions. Historical spill sites may be decades old, while other sites contain hydrocarbons from spills and leaks that occurred more recently (i.e., a few days to a few years). Depending on soil and climate conditions, the chemicals from historical spills may have been impacted by various amounts of weathering, natural biodegradation and/or sequestration.

Bioavailability: Bioavailability is sometimes considered as synonymous with toxicity to one or another species, sometimes as equivalent to biodegradation by microorganisms, and sometimes as synonymous with uptake or assimilation. A compound may be assimilated and, although toxic, may not cause injury because it is not transported to the tissue, cell or intracellular site where the toxicity can be expressed. A chemical may be taken up into microbial cells but still not be biodegraded because that organism does not contain the requisite catabolic enzymes. Uptake or assimilation is thus a better means of assessing bioavailability, but because of the few studies of uptake *per se* and the many more of toxicity and biodegradation, the term bioavailability also should be used to include toxicity and biodegradation.

Biodegradation: Biodegradation (sometimes considered as a weathering process) is the biological conversion of an organic compound to products of simpler structure. For complex mixtures of hydrocarbons, biodegradation follows a pattern in which the more readily biodegradable hydrocarbons are oxidized before more recalcitrant hydrocarbons. The amount of prior biodegradation that has occurred in a contaminated soil can be quantitatively assessed by fingerprinting the hydrocarbons in a soil. For example, gas chromatography can be used to observe the loss of n-alkanes (the most biodegradable hydrocarbons) in comparison to branched alkanes. Gas chromatograph-mass spectrophotometer (GC-MS) can be used to observe changes in the profiles of polycyclic aromatic hydrocarbons (PAHs), since the parent PAHs are more biodegradable than their alkylated homologues^{1,2}.

Effective Carbon Number: The EC number is a unitless value representing the carbon atom equivalency to the n-alkanes based upon the target compounds retention time in boiling point gas chromatograph column.

Environmentally Acceptable Endpoint: Environmentally acceptable endpoints for soil are the concentrations of chemical contaminants that are judged to be acceptable (i.e., they do not pose an unacceptable human health or environmental risk) by a regulatory agency following an analysis of site-specific or chemical-specific concentrations remaining in site soils.

Massachusetts Department of Environmental Protection (MADEP) Approach: The MADEP based its TPH fractions on chemical structure, carbon number and structure activity relationships. The MADEP aliphatic fractions include C₅ – C₈, C₉ – C₁₈ and C₁₉ – C₃₆ carbon ranges. The aromatic fractions include the C₉ – C₁₀ and C₁₁ – C₂₂ carbon ranges. The aromatic C₆ – C₈ compounds are evaluated individually. The MADEP uses two distinct analytical protocols to analyze petroleum hydrocarbons in water and soil: (1) the volatile petroleum hydrocarbons protocol for light aliphatic and aromatic fractions; and (2) the extractable petroleum hydrocarbons protocol for the medium to heavy aliphatic and aromatic fractions.

Petroleum Hydrocarbons: Petroleum hydrocarbons are organic compounds comprised of carbon and hydrogen atoms arranged in varying structural configurations that, in the broadest sense, can be divided into aliphatics and aromatics families. There are three main classes of aliphatic compounds, the alkanes, alkenes and cycloalkanes. The alkanes are the simplest structures consisting of single, straight chain carbon-carbon bonds. The alkenes consist of hydrocarbon structures that contain one or more double bonds between the carbon atoms. The cycloalkanes are alkanes where carbon atoms form cyclic structures. There are also three main classes of aromatic compounds, monoaromatics, diaromatics and PAHs. The monoaromatics consist of one ring with either six hydrogen groups or a combination of alkyl and hydrogen groups attached to a six-carbon aromatic (benzene) ring. Diaromatics have two fused benzene rings as their basic structure with eight hydrogen or alkyl groups attached to the rings. PAHs consist of more than two fused benzene rings as a structural characteristic. In general, alkyl-substituted PAHs are predominant in petroleum mixtures that contain these compounds.

Risk-Based Corrective Action (RBCA): The RBCA process involves the integration of site assessment, remedial action response and site monitoring with U.S. EPA-recommended risk and exposure assessment practices. RBCA provides a process through which corrective action decisions are made in a consistent manner that is protective of human health and the environment. The RBCA process recognizes that chemical release sites vary widely in complexity, physical and chemical characteristics, and in the risk they pose to human and ecological receptors. Consequently, the RBCA process is implemented in a tiered approach, involving increasingly sophisticated levels of data collection and analysis. The process usually begins at Tier 1, where risk-based screening levels that are calculated using non-site-specific information/data are applied to achieve quick, regulatory-agency approved closure. If Tier 1 results indicate an unacceptable risk to human health and/or the environment, the RBCA process moves on to a Tier 2 and/or Tier 3 evaluation, using increasing amounts of site-specific information/data until a corrective action decision is made leading to site closure.

Sequestration: Sequestration results from the binding of chemicals to or within soil particles. The extent of sequestration may be influenced by time, soil organic matter content, clay content, cycles of wetting and drying, and chemical type and properties^{3,4}. Sequestration has an influence on the extent and rate of biodegradation and can decrease the bioavailability of organic compounds to soil organisms, thus reducing toxicity of the contaminated soils.

Total Petroleum Hydrocarbons: Total petroleum hydrocarbons consist of mixtures of aliphatic and aromatic compounds in a collection of boiling point fractions ranging from crude oil (a wide range of light, medium and heavy hydrocarbon compounds from five to more than 36 carbons) to gasoline (light aliphatic and aromatic hydrocarbon compounds less than 12 carbons).

Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) Approach: The TPHCWG approach included an analysis of physical-chemical properties (e.g., molecular weight, boiling point, vapor pressure and water solubility) of complex hydrocarbon mixtures to identify subsets (called fractions) that behave similarly in environmental media. The aliphatic hydrocarbon fractions with similar fate and transport characteristics were identified as: EC₅ – EC₆, EC_{>6} – EC₈, EC_{>8} – EC₁₀, EC_{>10} – EC₁₂, EC_{>12} – EC₁₆, EC_{>16} – EC₂₁ and EC_{>21} – EC₃₅. Similarly, the aromatic hydrocarbon fractions with similar fate and

transport characteristics were identified as: $EC_{>6} - EC_8$, $EC_{>8} - EC_{10}$, $EC_{>10} - EC_{12}$, $EC_{>12} - EC_{16}$, and $EC_{>16} - EC_{21}$. These aliphatic and aromatic hydrocarbon fractions are detected in site soils using the Direct Analytical Method developed by the TPHCWG with assistance from the Shell Development Company.

Toxicity: Toxicity is the ability of a chemical to cause an adverse health effect, such as cancer or poisoning. Commonly, toxicity test results are presented as a concentration that elicits a certain response or effect on the test organisms, such as the concentration or dose in an acute exposure that is lethal to 50% of the test population (LC_{50} or LD_{50} , respectively). Another toxicity test result that is commonly used is the no observed adverse effect level or the lowest observed adverse effect level.

Weathering: Weathering refers to the result of biological, chemical and physical processes that can affect the type of hydrocarbons that remain in a soil. For instance, during weathering, there can be hydrocarbon losses from soil due to volatilization of the lower boiling point fractions of saturates (aliphatics) and aromatics and/or the loss of water soluble low-boiling point fractions of aromatic hydrocarbons due to leaching.

REFERENCES

1. Elmendorf, D. L., Haith, C. E., Douglas, G. S., and Prince, R. C. 1994. Relative rates of biodegradation of substituted polyaromatic hydrocarbons. In: Bioremediation of Chlorinated and PAH Compounds. Hinchee, R. E., Semprini, L, and Ong, S. K., eds. CRC Press, Boca Raton, FL. pp. 188-202.
2. McMillen, S. J., Gray, N. R., Kerr, J. M., Requejo, A. G., McDonald, T. J., and Douglas, G. S. 1995. Assessing bioremediation of crude oil in soils and sludges. In: Monitoring and Verification of Bioremediation. Hinchee, R.E., Douglas, G.S., and Ong, S.K., eds. Battelle Press, Columbus, OH. pp. 91-99.
3. Loehr, R. C. and Webster, M. T. 1996. Behavior of fresh vs. aged chemicals in soil. J. Soil Contam. 5:361-383.
4. White, J. C., Kelsey, J. W., Hatzinger, P. B., and Alexander, M. 1997. Factors affecting sequestration and bioavailability of phenanthrene in soils", Environ. Toxicol. Chem. 16:2040-2045.